diphenyldiacetic acid, m. p. above 300°. Recrystallized for analysis from aqueous ethanol. *Anal.* Calcd. for $C_{30}H_{36}O_6$: C, 74.76; H, 5.43. Found: C, 74.82; H, 5.78. Iodination with potassium triiodide in alkaline solution yielded a brown crystalline substance which could not be purified either by the use of sodium carbonate solution or organic solvents. The product gave a positive test for halogen and was for the most part alkali soluble. Iodination with iodine chloride in acetic acid also gave a dark crystalline product which could not be purified.

Summary

A series of α-naphthyl and α-tetralyl derivatives of halogenated arylpropionic and acrylic acids have been prepared. Preliminary pharmacological study in animals indicates that these compounds do not possess cholecystographic properties.

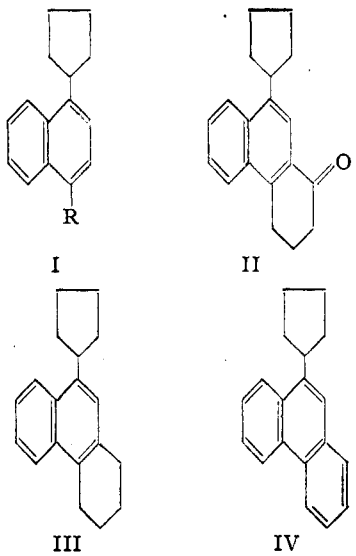
BLOOMFIELD, N. J. RECEIVED APRIL 10, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Preparation and Reactions of 1-Cyclopentylnaphthalene

BY W. E. BACHMANN AND L. H. KLEMM[1]

In a study of antimalarials carried out during the war years in coöperation with the Committee on Medical Research we prepared 1-cyclopentylnaphthalene (I, R = H) and studied some of its reactions. No mention of the hydrocarbon or its derivatives was found in the literature other than the report of Pokrovskaya and Sushchik[2] that a "monocyclopentylnaphthalene" fraction of unknown structure was isolated from the Friedel–Crafts condensation of cyclopentene with naphthalene.



I II

III IV

We prepared 1-cyclopentylnaphthalene by hydrogenation of the known 1-(1′-naphthyl)-1-cyclopentene, which results from the reaction between 1-naphthylmagnesium bromide and cyclopentanone followed by dehydration of the intermediate tertiary alcohol. The addition of hydrogen to the olefin occurred readily and almost quantitatively at low pressure and room temperature in acetic acid solution in the presence of Adams catalyst. This behavior is in sharp contrast to that of the homologous compound 1-(1′-naphthyl)-1-cyclohexene, which, as reported by Cook and Lawrence,[3] strongly resisted the addition of hydrogen under the same conditions.

Sulfonation, acetylation and succinoylation of 1-cyclopentylnaphthalene were effected by means of chlorosulfonic acid in carbon tetrachloride, acetyl chloride and aluminum chloride in carbon disulfide, and succinic anhydride and aluminum chloride in nitrobenzene, respectively. The substituents introduced by these reactions were all shown to occupy the 4-position of the naphthalene nucleus by means of a series of four separate steps: (1) proof of the equivalence of the positions occupied by the sulfonic acid and the acetyl groups; (2) a similar proof for the acetyl and succinoyl groups; (3) proof that the succinoyl group occupied either the 3- or the 4-position; (4) proof that the acetyl group occupied an alpha position.

For the first part of this proof the sulfonic acid group was replaced successively by a bromo and a cyano group. By a Grignard reaction with methylmagnesium iodide the cyano derivative was converted into the acetyl compound which was identical with that obtained by acetylation. The production of the same acid by hydrolysis of the cyano compound and by hypochlorite oxidation of the acetyl derivative confirmed the previous result.

For the second part the acetyl compound (I, R = $COOH_3$) was brominated in ether to the ω-bromoacetyl derivative, which on reaction with sodio-malonic ester, hydrolysis, and decarboxylation gave the succinoyl derivative.

In the third part of the proof the succinoyl

(1) From the Ph.D. dissertation of L. H. Klemm, 1945.

(2) Pokrovskaya and Sushchik, *J. Gen. Chem. (U. S. S. R.)*, **9**, 2291 (1939); [*C. A.*, **34**, 5433 (1940)].

(3) (a) Cook and Lawrence, *J. Chem. Soc.*, 1431 (1936). Compare (b) Bachmann and Kloetzel, THIS JOURNAL, **60**, 2204 (1938); (c) Bergmann and Bergmann, *ibid.*, **62**, 1699 (1940); and (d) Bergmann and Szmuszkowicz, *ibid.*, **69**, 1367 (1947), for differences in the reactivities of these olefins to maleic anhydride in the Diels-Alder reaction, and (e) Bachmann and Deno, *ibid.*, **71**, 3062 (1949), for differences in the ultraviolet absorption spectra. See (h) Orchin and Reggel, *ibid.*, **69**, 505 (1947), for the reduction of 1-(1′-naphthyl)-1-cyclohexene. Further investigations on the addition of hydrogen to these and other 1-aryl-1-cycloalkenes are being carried out by L. H. K.

derivative was reduced by the Clemmensen method and the reduced acid was cyclized *via* the acid chloride to 1-keto-9-cyclopentyl-1,2,3,4-tetrahydrophenanthrene (II). Clemmensen reduction of the cyclic ketone yielded 9-cyclopentyl - 1,2,3,4 - tetrahydrophenanthrene (III), which was dehydrogenated by palladium–charcoal to 9-cyclopentylphenanthrene (IV). The last hydrocarbon was identical with the product prepared by reduction of the known 1-(9′-phenanthryl)-1-cyclopentene. The result showed that the succinoyl group was in either the 4-position (as shown in I, R = $COCH_2CH_2COOH$) or the 3-position of the keto acid obtained from 1-cyclopentylnaphthalene.

In the final step of the proof the acetyl derivative of 1-cyclopentylnaphthalene was reduced to 1-cyclopentyl-4-ethylnaphthalene (I, R = C_2H_5) in which the position of the cyclopentyl group was definitely known. The same compound was prepared from 1-ethylnaphthalene by sulfonation, replacement of the sulfonic acid group by bromine, and replacement of the bromine by the cyclopentyl group by the procedure used for the preparation of 1-cyclopentylnaphthalene. This result showed that the acetyl group was in an alpha position; hence, the 3-position was eliminated as a possible solution and the 4-position was thereby established for the position of the groups entering the 1-cyclonaphthalene structure.

4-Cyclopentyl-1-naphthaleneacetic acid was prepared in good yield by the Willgerodt reaction on the acetyl derivative. Beckmann rearrangement of the oxime of the acetyl derivative by means of phosphorus pentachloride produced the acetylamino derivative, which was hydrolyzed to 4-cyclopentyl-1-aminonaphthalene hydrochloride.

The antimalarial activities of compounds which were prepared from the bromoacetyl derivative (I, R = $COCH_2Br$) and the amino derivative (I, R = NH_2) are reported in the survey of antimalarial drugs of the Committee on Medical Research.[4]

Experimental

1-Cyclopentylnaphthalene (I, R = H).—1-(1′-Naphthyl)-1-cyclopentene was prepared according to the directions of Bachmann and Kloetzel[3b] as modified by Kleene.[5] The Grignard reagent from 1-bromonaphthalene (363 g.) was treated with cyclopentanone (160 g.) and the crude tertiary alcohol was dehydrated directly with anhydrous formic acid and fractionally distilled twice; b. p. 122–124° at 0.1 mm.; yield 206 g.

A solution of 50 g. of the unsaturated hydrocarbon in 125 ml. of glacial acetic acid was shaken with Adams catalyst (0.7 g.) under hydrogen at 1–2 atmospheres pressure and room temperature until an equimolar quantity of hydrogen had been absorbed (five to fifteen hours). The filtered solution after dilution with four volumes of water was extracted with ether and the ethereal extract was washed with aqueous sodium carbonate. The 1-cyclopentylnaphthalene (48.6–50 g.), which distilled at 120–124° and 0.05 mm., did not decolorize cold, dilute potassium permanganate solution. Pokrovskaya and Sushchik[2] reported a boiling point of 134–135° at 1.5 mm. for a "monocyclopentylnaphthalene" of unknown structure.

The **picrate** of 1-cyclopentylnaphthalene crystallized from absolute ethanol in yellow-orange needles; m. p. 93.5–94.5°.

Anal. Calcd. for $C_{21}H_{19}N_3O_7$: N, 9.9. Found: N, 10.1.

When hydrogenation was effected by shaking an absolute ethanolic solution (150 ml. of solvent per 50 g. of olefin) with Raney nickel under conditions of temperature and pressure identical to those used previously, it was necessary to replace the spent catalyst once or twice in order to obtain absorption of the theoretical amount of hydrogen.

4-Cyclopentyl-1-naphthonitrile (I, R = CN).—A solution of 10 g. of 1-cyclopentylnaphthalene in 25 ml. of carbon tetrachloride was kept at −4° or lower in an ice–salt-bath while 6.42 g. of chlorosulfonic acid (covered by 5 ml. of carbon tetrachloride) was added dropwise with stirring. Considerable hydrogen chloride was evolved. After an additional half-hour of stirring the cooling bath was removed, and 25 ml. of water was added. The layers were separated and the carbon tetrachloride layer was extracted with water once more. The combined aqueous layers were stirred rapidly while 25% potassium hydroxide was added dropwise to slight alkalinity. The colorless precipitate of the potassium salt of 1-cyclopentylnaphthalene-4-sulfonic acid was collected and dried to constant weight at 60°; weight, 13.9 g.

The sulfonic acid group was replaced by bromine *via* the method used by Fieser and Bowen for the preparation of 1-methyl-4-bromonaphthalene.[6] To a rapidly stirred solution of 10 g. of the preceding potassium salt in 200 ml. of water at 70° a solution of 5.8 g. of bromine and 8.6 g. of sodium bromide in 30 ml. of water at 55° was added in one portion. The reaction was stopped after exactly thirty seconds by the addition of excess saturated sodium bisulfite solution. The mixture was cooled to room temperature and the precipitated liquid, presumably 1-cyclopentyl-4-bromonaphthalene, was extracted with carbon tetrachloride and purified by evaporative distillation at 0.05 mm.; weight, 7.5 g.

A mixture of 4 g. of the bromo compound, 2.5 g. of cuprous cyanide, and 2.5 ml. of anhydrous pyridine was heated under reflux in a bath maintained at 203–208° for twenty-four hours. When the warm mixture was poured into 100 ml. of 15% aqueous ammonia, the nitrile solidified. From the precipitate which was collected by filtration and dried, the nitrile was extracted with hot acetone. Evaporative distillation of the product at 0.01 mm. afforded 3.1 g. of 4-cyclopentyl-1-naphthonitrile, which crystallized from acetone in colorless prisms; m. p. 79–80.5°; yield, 2.9 g. (91%). One further recrystallization of a sample raised the melting point to 80–81°.

Anal. Calcd. for $C_{16}H_{15}N$: N, 6.3. Found: N, 6.2.

1-Cyclopentyl-4-acetylnaphthalene (I, R = $COCH_3$). (a) **By Acetylation of 1-Cyclopentylnaphthalene.**—To a stirred suspension of 180 g. of anhydrous aluminum chloride in 1100 ml. of carbon disulfide 95.5 g. of freshly distilled acetyl chloride was added dropwise. After ten minutes the mixture was cooled to about 0° in an ice-bath and a solution of 100 g. of 1-cyclopentylnaphthalene in 300 ml. of carbon disulfide was added dropwise over a period of nine hours. Stirring and cooling were continued eighteen hours longer. The chocolate-colored complex was collected rapidly by suction filtration, washed with a small amount of carbon disulfide, and added slowly to a stirred mixture of ice and water. The ketone which was purified by distillation (b. p. 179–181° at 0.1 mm.) crystallized completely after several weeks in a refrigerator; yield, 93–98 g. After two recrystallizations from methanol a sample formed practically colorless prisms; m. p. 36–37°.

(4) "A Survey of Antimalarial Drugs, 1941–1945," F. Y. Wiselogle, Editor, Edwards Bros., Ann Arbor, Michigan, 1946.

(5) Kleene, THIS JOURNAL, **63**, 631 (1941).

(6) Fieser and Bowen, *ibid.*, **62**, 2103 (1940).

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.5; H, 7.6.

The **picrate** crystallized from absolute ethanol in fine yellow needles; m. p. 82–83°.

Anal. Calcd. for $C_{23}H_{21}O_8N_3$: N, 8.99. Found: N, 9.15.

The **semicarbazone** crystallized from 80% ethanol in colorless prisms; m. p. 197–198°.

Anal. Calcd. for $C_{18}H_{21}ON_3$: N, 14.2. Found: N, 13.9.

(b) **From 4-Cyclopentyl-1-naphthonitrile.**—A solution of 1 g. of the nitrile in 20 ml. of benzene was refluxed for ten hours with the Grignard reagent prepared from 1.14 g. of methyl iodide in 20 ml. of ether. The cooled reaction mixture was treated with saturated ammonium chloride solution; the ketimine was extracted into excess cold concentrated hydrochloric acid, and the diluted solution was refluxed for forty-five minutes. The ketone which separated was evaporatively distilled at 0.01 mm.; yield, 0.72 g. (67%). The picrate melted at 81–82° alone and when mixed with the picrate obtained in part (a).

4-Cyclopentyl-1-naphthoic Acid. (a) **By Oxidation of 1-Cyclopentyl-4-acetylnaphthalene.**—To a solution of 2 g. of the preceding acetyl derivative in 30 ml. of dioxane at 60–70° was added 50 ml. of warm sodium hypochlorite solution prepared according to Newman and Holmes.[7] The mixture became homogeneous when stirred mechanically for two and one-half hours at 60–70°. The cooled solution was poured slowly with stirring into a mixture of concentrated hydrochloric acid, ice and sodium bisulfite; m. p. 174.5–176°; yield, 2 g. (99%). One recrystallization of a sample from ethyl acetate gave colorless prisms; m. p. 178–179°.

(b) **By Hydrolysis of 4-Cyclopentyl-1-naphthonitrile.**—A mixture of 0.7 g. of the nitrile, 15 g. of potassium hydroxide, and 50 ml. of methanol was refluxed for six days until evolution of ammonia had ceased. Removal of the solvent and acidification produced the crude acid which was further purified through solution in warm 5% sodium bicarbonate, filtration to remove silica, and three washings with ether to remove color and unreacted nitrile; m. p. 176–177°; yield, 0.53 g. (70%). Two recrystallizations of a sample from ethyl acetate produced colorless prisms; m. p. 180.5–181.5°. A mixed melting point of the once-recrystallized products from parts (a) and (b) showed no depression.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.8; H, 6.8.

β-(4-Cyclopentyl-1-naphthoyl)-propionic Acid (I, R = $COCH_2CH_2COOH$). (a) **Succinoylation of 1-Cyclopentylnaphthalene.**—A solution of 93 g. of anhydrous aluminum chloride in 170 ml. of nitrobenzene was prepared below 20°. The temperature was kept at 0–5° during the addition of 30 g. of succinic anhydride followed by a solution of 50 g. of 1-cyclopentylnaphthalene in 80 ml. of benzene (added dropwise over a period of two and one-half hours). The reaction mixture was stirred in the ice-bath for six hours longer and then refrigerated overnight. The keto acid remaining after steam distillation of the hydrolyzed mixture was triturated with hydrochloric acid, dissolved in excess warm 5% sodium bicarbonate (Norit), and re-precipitated; weight, 67 g. One recrystallization of a sample from glacial acetic acid gave colorless prisms, m. p. 130–132°. Two further recrystallizations, first from ethyl acetate–ligroin and then from ethyl acetate alone, raised the melting point to 131.5–132.5°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.0; H, 6.8. Found: C, 77.2; H, 6.8.

(b) **From 1-Cyclopentyl-4-acetylnaphthalene.**—An ice-cold solution of 2 g. of crude ketone in 70 ml. of anhydrous ether to which a solution of 0.44 ml. of bromine in 20 ml. of ether had been added was placed in sunlight; in two minutes the bromine color disappeared. The colorless solution was washed, dried, and evaporated and a solution of the residual ω-bromoacetyl compound in 20 ml. of benzene was added to a suspension of sodiomalonic ester which had been prepared by refluxing 0.42 g. of powdered sodium and 4.2 ml. of diethyl malonate in 75 ml. of benzene for six hours. After standing at room temperature for two days, the mixture was refluxed for one hour. By hydrolysis and decarboxylation of the product, 0.75 g. of acid was obtained, which after recrystallization from dilute acetic acid and from ethyl acetate–petroleum ether melted at 129.5–131.5°, alone and when mixed with the once-recrystallized acid from part (a).

The bromoketone was also prepared by adding 13.5 g. of bromine dropwise in the course of an hour to a stirred, chilled (ice–salt-bath) solution of 20 g. of 1-cyclopentyl-4-acetylnaphthalene in 700 ml. of anhydrous ether containing 0.5 g. of anhydrous aluminum chloride. After being stirred for one-half hour without cooling, the mixture was concentrated to half its volume, washed with sodium bicarbonate, dried, and evaporated. The liquid bromoketone darkened on standing. The **quaternary pyridinium bromide**, which formed in a few minutes from the bromoketone and excess anhydrous pyridine, was triturated with ether, filtered and washed with ether; m. p. about 236° dec. Three recrystallizations from methanol gave colorless, micaceous platelets with the same decomposition point.

Anal. Calcd. for $C_{22}H_{22}ONBr$: N, 3.54; Br, 20.2. Found: N, 3.54; Br, 20.2.

γ-(4-Cyclopentyl-1-naphthyl)-butyric Acid.—A solution of 69.8 g. of the crude preceding keto-acid in 400 ml. of toluene was added to a mixture of 300 g. of amalgamated mossy zinc, 560 ml. of glacial acetic acid, and 560 ml. of concentrated hydrochloric acid, and the whole was refluxed for twenty-four to thirty-six hours, during which time an additional 400 ml. of concentrated hydrochloric acid was added in three or four portions. The mixture was poured into an equal volume of water, the layers were separated, and the aqueous layer was extracted twice with benzene. The reduced acid distilled at 236–238° and 1 mm.; m. p. 107–114°; yield, 57.4 g. Three recrystallizations of a sample from 95% ethanol gave colorless needles; m. p. 117–118°.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.8; H, 7.8. Found: C, 80.9; H, 7.7.

1-Keto-9-cyclopentyl-1,2,3,4-tetrahydrophenanthrene (II).—To 20.5 g. of phosphorus pentachloride was added 25 g. of the powdered, unrecrystallized preceding acid. After the somewhat vigorous bubbling had subsided, the mixture was warmed gently with occasional swirling for one to two hours. After the removal of volatile material under reduced pressure at 80–90°, a chilled solution of the acid chloride in 100 ml. of benzene was treated with a solution of 46 g. of anhydrous stannic chloride in 20 ml. of benzene (added rapidly with vigorous mechanical stirring). After an additional fifteen minutes of stirring the green-black reaction product was hydrolyzed and the cyclic ketone, which was isolated in the usual manner, was distilled at 210–245° and 0.8 mm.; m. p. 82–87°; yield, 16 g. Two recrystallizations of a sample from methanol gave large colorless prisms; m. p. 90–91°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.3; H, 7.6. Found: C, 86.3; H, 7.7.

The **oxime**, prepared in a mixture of absolute alcohol and pyridine, formed colorless prisms after three recrystallizations from 95% ethanol; m. p. 201–202°.

Anal. Calcd. for $C_{19}H_{21}ON$: N, 5.01. Found: N, 5.05.

9-Cyclopentyl-1,2,3,4-tetrahydrophenanthrene (III).—Ten grams of the cyclic ketone was reduced by the method used on the keto acid. The hydrocarbon which distilled at 157–161° and 0.2 mm. crystallized in practically colorless prisms when scratched; m. p. 40–46°; yield, 8.3 g. (88%). Three recrystallizations of a sample from acetone–methanol raised the melting point to 49–50°.

Anal. Calcd. for $C_{19}H_{22}$: C, 91.1; H, 8.0. Found: C, 91.2; H, 8.8.

(7) Newman and Holmes, *Org. Syntheses*, **17**, 65 (1937).

The **picrate** of the hydrocarbon crystallized from absolute ethanol in orange needles; m. p. 143–144°.

Anal. Calcd. for $C_{25}H_{25}O_7N_3$: N, 8.76. Found: N, 8.92.

9-Cyclopentylphenanthrene. (a) Hydrogenation of 1-(9'-Phenanthryl)-1-cyclopentene.—To the Grignard reagent from 10 g. of 9-bromophenanthrene, 1 g. of magnesium and 30 ml. of ether was added (with cooling in an ice–salt-bath) 15 ml. of benzene and then, dropwise, a solution of 3.62 g. of cyclopentanone in 15 ml. of reagent benzene. The mixture was swirled to dissolve the white complex which formed where the drops fell, allowed to stand in an ice-bath for thirteen hours, and hydrolyzed with ice and aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with ether. After removal of the ether from the dried extracts, the residue was poured with swirling into 40 ml. of anhydrous formic acid. After ten minutes at room temperature, the mixture was warmed on a steam-bath for five minutes, poured into 160 ml. of water, extracted with benzene, and the extracts were washed with dilute sodium hydroxide. The 1-(9'-phenanthryl)-1-cyclopentene distilled at 158–161° and 0.05 mm.; yield, 5.6 g. (59%) (reported,[8] 20% yield; b. p. 185° at 0.85 mm.). The picrate crystallized from absolute ethanol in orange needles; m. p. 120–121° (reported,[8] red needles with m. p. 120°).

A solution of 4 g. of the unsaturated hydrocarbon in 50 ml. of glacial acetic acid was shaken with 0.2 g. of Adams' catalyst and hydrogen at one to two atmospheres pressure for ten hours. As soon as the calculated quantity of hydrogen had been absorbed, the solution deposited a solid. The mixture was poured into 200 ml. of water, and the product after isolation with benzene was evaporatively distilled at 0.05 mm.; m. p. 54–58°; yield, 3.85 g. (95%). The **9-cyclopentylphenanthrene** crystallized from 97% ethanol in colorless needles; m. p. 61.5–62.5°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.6; H, 7.4. Found: C, 92.5; H, 7.3.

The **picrate** crystallized from absolute alcohol in yellow-orange needles; m. p. 124.5–125.5°.

Anal. Calcd. for $C_{25}H_{21}O_7N_3$: N, 8.84. Found: N, 9.00.

(b) Dehydrogenation of 9-Cyclopentyl-1,2,3,4-tetrahydrophenanthrene.—A mixture of 120 mg. of 9-cyclopentyl-1,2,3,4-tetrahydrophenanthrene and 18 mg. of palladium-charcoal[9] under an atmosphere of carbon dioxide was kept at 300° for twenty minutes and then at 300–320° for an additional fifteen minutes. The product after separation from the catalyst by evaporative distillation at 0.02 mm. melted at 56–58°; yield, 108 mg. (92%). The product and its picrate were identical with those described in part (a).

1-Cyclopentyl-4-ethylnaphthalene. (a) From 1-Cyclopentyl-4-acetylnaphthalene.—Clemmensen reduction of 50 g. of the ketone according to the procedure employed on the keto acid yielded 45.2 g. of 1-cyclopentyl-4-ethylnaphthalene as a liquid; b. p. 140–144° at 0.1 mm. The light yellow needles of the **trinitrobenzene complex** which were formed in absolute ethanol were collected by filtration and washed with ether; m. p. 112–113°.

Anal. Calcd. for $C_{23}H_{23}O_6N_3$: N, 9.61. Found: N, 9.32.

(b) From 1-Acetylnaphthalene.—Starting with 1-acetylnaphthalene and using the same procedures as given previously (but with slight variations as noted) the following successive transformations were carried out. Clemmensen reduction of 100 g. of 1-acetylnaphthalene produced 85.4 g. of 1-ethylnaphthalene. Treatment of 78 g. of this hydrocarbon with chlorosulfonic acid and then potassium hydroxide yielded 105.6 g. of the potassium sulfonate. Treatment with aqueous bromine–sodium bromide at 50–55° for fifteen seconds converted 60 g. of the potassium salt to 38.5 g. of bromo derivative; b. p. 134–136° at 0.4 mm. The reaction of the Grignard reagent from 30 g. of the bromo compound with 11.5 g. of cyclopentanone, followed by dehydration of the crude carbinol with anhydrous formic acid gave 14.8 g. of 1-(4'-ethyl-1'-naphthyl)-1-cyclopentene; b. p. 148–150° at 0.09 mm. The **picrate** crystallized from absolute ethanol in orange needles; m. p. 101.5–102.5°.

Anal. Calcd. for $C_{23}H_{21}O_7N_3$: N, 9.31. Found: N, 9.40.

The **trinitrobenzene complex** crystallized from absolute ethanol in yellow-orange prisms; m. p. 112.5–113.5°. A mixed melting point of this trinitrobenzene complex with that in part (a) showed a depression of 1°.

Anal. Calcd. for $C_{23}H_{21}O_6N_3$: N, 9.65. Found: N, 9.44.

Four grams of the unsaturated hydrocarbon was hydrogenated in the presence of Adams catalyst as in the preparation of 1-cyclopentylnaphthalene. Evaporative distillation of the crude product at 0.05 mm. gave 3.38 g. of 1-cyclopentyl-4-ethylnaphthalene, the trinitrobenzene complex of which formed short yellow needles; m. p. 111.5–112.5°, unchanged on admixture with the corresponding complex from part (a).

4-Ethyl-1-naphthoic Acid.—The bromo derivative of 1-ethylnaphthalene was treated with cuprous cyanide and pyridine as in the preparation of 4-cyclopentyl-1-naphthonitrile except that the temperature was 215–230°. After the warm reaction mixture had been poured into ammonium hydroxide, the nitrile was extracted into ether. By evaporative distillation at 0.5 mm. the nitrile was obtained as a practically colorless liquid which showed no halogen by the Beilstein test; $n^{25}D$ 1.6161; yield, 3.6–3.8 g. from 5.1 g. of the bromo compound. Hydrolysis of 1 g. of the nitrile with methanolic potassium hydroxide by the procedure given previously for another nitrile yielded the acid, which crystallized from ethanol in colorless prisms; yield, 0.69 g.; m. p. 123.5–128°. After three more recrystallizations from aqueous ethanol the 4-ethyl-1-naphthoic acid melted at 132–133°.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 78.0; H, 6.0. Found: C, 78.0; H, 5.9.

Gattermann and Harris[10] reported a melting point of 132° for the acid obtained by hydrolysis of the product prepared from 1-ethylnaphthalene and carbamyl chloride. These authors offered no proof for the structure of the acid.

Willgerodt Reaction on 1-Cyclopentyl-4-acetylnaphthalene.—Following similar procedures[11] a mixture of 2 g. of the ketone, 10 ml. of ammonium polysulfide reagent, and 8 ml. of purified dioxane was heated in a sealed Pyrex tube at 169–172° for twenty-five hours. The cooled tube contained 1.94 g. of gray solid; m. p. 196–200°. After two recrystallizations from acetone–benzene a sample of the **4-cyclopentyl-1-naphthaleneacetamide** formed fine colorless needles; m. p. 208–209°.

Anal. Calcd. for $C_{17}H_{19}NO$: N, 5.53. Found: N, 5.37.

One g. of the crude amide was refluxed with a mixture of 30 ml. of glacial acetic acid, 10 ml. of concentrated hydrochloric acid, and 2 ml. of water for twenty-four hours. The crystals which separated on cooling were recrystallized from ethyl acetate; m. p. 165–168°; yield, 0.78 g. (78%). After three more recrystallizations the colorless needles of **4-cyclopentyl-1-naphthaleneacetic acid** melted at 171–172°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.5; H, 7.1.

Beckmann Rearrangement of 1-Cyclopentyl-4-acetylnaphthalene Oxime.—A mixture of 20 g. of 1-cyclopentyl-4-acetylnaphthalene, 20 g. of hydroxylamine hydrochloride, 100 ml. of absolute ethanol, and 100 ml. of dry pyridine was refluxed on a steam-bath for three hours. After the removal of the solvents in a current of air, the residue was triturated with water. The **oxime** crystallized from

(8) Bergmann and Bergmann, THIS JOURNAL, **59**, 1443 (1937).

(9) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

(10) Gattermann and Harris, *Ann.*, **244**, 57 (1888).

(11) Fieser and Kilmer, THIS JOURNAL, **62**, 1354 (1940).

methanol in colorless prisms; yield, 18.3–18.7 g. (86–88%); m. p. 149–150°. After two more recrystallizations of a sample, the m. p. was 152.5–153.5°.

Anal. Calcd. for $C_{17}H_{19}ON$: N, 5.53. Found: N, 5.35.

A chilled solution of 2 g. of the oxime in 40 ml. of benzene was treated with 2 g. of phosphorus pentachloride (added all at once), and the mixture was refluxed on a steam-bath for fifteen minutes. The precipitate obtained by hydrolysis with water and evaporation of the benzene weighed 1.31 g.; m. p. 156.5–157.5°. The product darkened slowly on standing in air and more rapidly on warming in a solvent in contact with air. After three recrystallizations from acetone (by cooling in an alcohol–Dry Ice-bath a solution saturated at room temperature) a sample of **4-cyclopentyl-1-acetylaminonaphthalene** formed a colorless prisms; m. p. 162–163°.

Anal. Calcd. for $C_{17}H_{19}ON$: N, 5.53. Found: N, 5.30.

The moist crude acetylamino compound prepared from ten times the quantities of materials used in the preceding directions was refluxed with a mixture of 700 ml. of ethanol and 45 ml. of concentrated hydrochloric acid on a steam cone under an atmosphere of carbon dioxide for twenty-four hours. The solvent was removed by distillation and the crystalline residue was recrystallized from 1.5 l. of water (Norit); yield, 9.4 g. Additional solid (1 g.) was obtained from the filtrate by making it basic with sodium hydroxide, extracting with ether and passing hydrogen chloride into the dried ethereal solution. The combined **4-cyclopentyl-1-naphthylamine hydrochloride** sublimed at 135–140° at 0.2 mm. as colorless crystals; m. p. above 260° dec.

Anal. Calcd. for $C_{15}H_{18}NCl$: N, 5.65. Found: N, 5.85.

Summary

1-Cyclopentylnaphthalene was prepared from 1-bromonaphthalene. The hydrocarbon was acetylated, succinoylated, and sulfonated in the 4-position. The three primary substitution products were converted to other 4-derivatives of the parent hydrocarbon.

9-Cyclopentylphenanthrene, 9-cyclopentyl-1,2,-3,4-tetrahydrophenanthrene, and some 1-ethyl-4-substituted-naphthalenes were synthesized.

ANN ARBOR, MICHIGAN RECEIVED MAY 10, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Decomposition of Lauroyl Peroxide in Benzene and Diethyl Ether

BY W. E. CASS

A variation in the rate of decomposition of benzoyl peroxide in different solvents has been observed by a number of investigators.[1-4] The increased rate in certain solvents has been ascribed to an "induced decomposition," in which radicals from the solvent (or peroxide) attack the undissociated peroxide. Inhibition of the induced decomposition by known inhibitors for free radical reactions (*e. g.*, oxygen) has been considered evidence for a free radical chain mechanism. Isolation of the products of reaction of benzoyl peroxide with certain aliphatic ethers[5] indicated the possibility of a simple two-step chain for the induced decomposition in these cases

$$C_6H_5COO\cdot + RH \xrightarrow{k_b} C_6H_5COOH + R\cdot \quad (b)$$

$$R\cdot + (C_6H_5COO)_2 \xrightarrow{k_c} C_6H_5COOR + C_6H_5COO\cdot \quad (c)$$

The present work was undertaken to find out if lauroyl peroxide, an aliphatic diacyl peroxide, also exhibited induced decomposition.[6]

(1) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946).
(2) Bartlett and Nozaki, *ibid.*, **69**, 2299 (1947).
(3) Cass, *ibid.*, **68**, 1976 (1946).
(4) Barnett and Vaughan, *J. Phys. & Colloid Chem.*, **51**, 926, 942 (1947).
(5) Cass, THIS JOURNAL, **69**, 500 (1947).
(6) Kharasch, Jensen and Urry, *J. Org. Chem.*, **10**, 386 (1945), postulated the following induced decomposition steps as part of their mechanism for the reaction of diacetyl peroxide with methyl chloroacetate

$$CH_3COO\cdot + (CH_3COO)_2 \longrightarrow CH_3COOCH_3 + CH_3COO\cdot + CO_2$$

$$CH_3\cdot + (CH_3COO)_2 \longrightarrow CH_3COOCH_3 + CH_3COO\cdot$$

Kinetic experiments at 30° indicated that lauroyl peroxide decomposed about eight times more rapidly in diethyl ether $k_1 \sim 0.007$ hr.$^{-1}$ than in benzene $k_1 \sim 0.0009$ hr.$^{-1}$. In both solvents the reactions appeared to be first order. Data from the kinetic experiments are listed in Table I. In each case the first order rate constant and the inhibition period were obtained from the plot of the data shown in Fig. 1.

TABLE I

DECOMPOSITION OF LAUROYL PEROXIDE IN SOLVENTS AT 30 ± 0.2°

Solvent	Total time, hr.	a	$a - x$	Inhib., hr.	k_1, hr.$^{-1}$
Ether	218	0.0515	0.0121	14	0.0072
Ether	217.5	.1020	.0238	12	.0072
Ether	211.7	.2010	.0515	11	.0068
Benzene	362	.2020	.1462	20	.00092

TABLE II

PRODUCTS OF REACTION OF LAUROYL PEROXIDE WITH DIETHYL ETHER AT ~37°

Product	Approx. yield, mole per mole peroxide dec.
Carbon dioxide	0.92[a,b], 0.8[c]
Hendecane	.84[d]
1-Ethoxyethyl laurate	.88,[e] 0.84[d]
Acid (lauric ?)	.037[b]
Ester (unknown)	.16[a,b,e]

[a] Calcd. from (alkaline) sapon. equiv. of ether-free residue. [b] Calcd. from neut. equiv. of residue. [c] Detd. by absorption in Ascarite. [d] Yield of crude product isolated. [e] Calcd. from (acid) sapon. equiv. of residue.