Alkylperylenes.[1] The Isomeric Ethylperylenes[2]

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Perylene has been acylated by the Friedel–Crafts method to furnish C-3 monoacylperylenes in good yield. A general scheme for the preparation of C-2 perylene derivatives has been developed. The alkylation of perylene with butyllithium and ethyllithium has furnished 1-alkylperylenes in fair yields while methylation afforded low yields of 1-methylperylene.

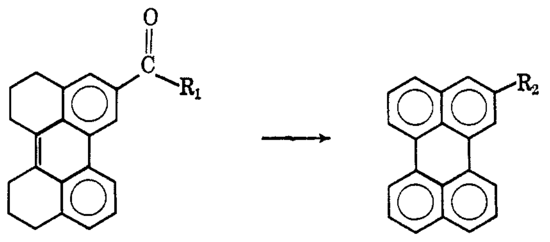
Perylene (1) is known for its high reactivity in electrophilic aromatic substitutions.[3] Buu Hoi and Dewar have described experimental conditions for the formylation[4] and nitration[5] of perylene at position 3. With the exception of Diels–Alder addition of maleic anhydride at C-1 and C-12 to form a stable adduct,[6] substitutions or additions to perylene at positions other than C-3 had not been reported until recently when the alkylation of perylene at C-1 with *n*-butyllithium was described.[7] The scope and mechanism of alkylation of aromatic hydrocarbons by butyllithium reagents have been studied by Dixon and co-workers.[8]

The objects of this paper are (1) to describe general methods for syntheses of C-2 and C-3 alkylperylenes *via* Friedel–Crafts acylations; (2) to present the evidence which supports the structures of the isomeric ethylperylenes; (3) to indicate the limitations on the generality of alkylation of perylene by several organolithium reagents.

Syntheses.—Perylene was converted into 3-acetylperylene (54%) and 3-hexanoylperylene (63%) by Friedel–Crafts acylations in chlorobenzene. Unreacted 1 (19–27%) and isomeric diacylperylenes (12–15%) were isolated. If monosubstitution occurred at C-1 or C-2, the maximum total amount of such isomeric ketones was less than 5%. Wolff–Kishner reduction of these ketones furnished 3-ethylperylene (91%) and 3-*n*-hexylperylene (90%). For structure proof, known perylene-3-carbonyl chloride[9] was transformed into authentic 3-*n*-hexanoylperylene with dipentyl cadmium.

1,2,3,10,11,12-Hexahydroperylene[10,11] (**5**, HHP) was prepared by catalytic hydrogenation of perylene. Friedel–Crafts acylations of **5** in chlorobenzene at 0° furnished mixtures of all three possible isomeric ketones. The major product (60.8%) of hexanoylation was 5-hexanoyl-1,2,3,10,11,12-HHP, as shown by transformations to perylene derivatives which are isomeric with known C-3 compounds.[12] See Scheme I. In like manner, acetylation occurred primarily at the 5 position, yielding 5-acetyl-1,2,3,10,11,12-HHP. Treatment of this ketone with palladium on charcoal gave 2-ethylperylene, the nmr spectrum of which showed four aromatic hydrogens at lowest field from tetramethylsilane corresponding to the C-1, -6, -7, and -12 protons. In contrast, the nmr spectrum for 1-ethylperylene (prepared by reaction of perylene with ethyllithium) integrated properly for only three aromatic protons of this type.

Scheme I



6a, $R_1 = CH_3$
b, $R_1 = n\text{-}C_5H_{11}$
c,[a] $R_1 = OH$

7a, $R_2 = CH_2CH_3$
b, $R_2 = COC_5H_{11}$
c, $R_2 = COOH$

[a] Obtained by haloform oxidation of **6a**.

The alkylation of perylene at C-1 with *n*-butyllithium has been described.[7] If the structure assignment of the major product in Friedel–Crafts acylation of hexahydroperylene is correct, alkylation of **1** with ethyllithium should furnish the third ethylperylene isomer directly. Refluxing of equimolar amounts of ethyl-

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(1) Abstracted in part from the Ph.D. thesis of H. E. Zieger, The Pennsylvania State University, Jan 1961; *Dissertation Abstr.*, **22**, 84 (1962).

(2) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts of Papers, p 46S.

(3) (a) P. H. Gore, in "Friedel Crafts and Related Reactions," Vol. III, part 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y. 1964, Chapter XXXI, p 81; (b) E. Clar, "Polycyclic Hydrocarbons," Vol. II, Academic Press Inc., N. Y., 1964, pp 24–33.

(4) N. P. Buu-Hoi and C. T. Long, *Rec. Trav Chim.*, **75**, 1221 (1956).

(5) M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956).

(6) E. Clar, *Ber.*, **65**, 846 (1932); E. Clar, *ibid.*, **82**, 53 (1949); E. Clar and M. Zander, *J. Chem. Soc.*, 4616 (1957).

(7) H. E. Zieger and J. E. Rosenkranz, *J. Org. Chem.*, **29**, 2469 (1964).

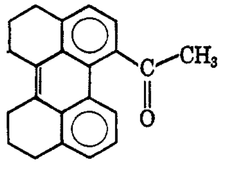
(8) J. A. Dixon and D. H. Fishman, *J. Am. Chem. Soc.*, **85**, 1356 (1963); J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, 613 (1964).

(9) Perylene-3-carboxylic acid is known by its method of preparation from 3,4,9,10-perylenetetracarboxylic 3,4-9,10-dianhydride; see Experimental Section and ref 25.

(10) (a) A. Zinke and E. Unterkreuter, *Monatsh.*, **40**, 405 (1919); A. Zinke and O. Benndorf, *ibid.*, **59**, 241 (1932); **64**, 87 (1934); (b) S. Friedman, S. Metlin, A. Svedi, and I. Wender, *J. Org. Chem.*, **24**, 1287 (1959).

(11) C. Hua-chih and H. Conrad-Billroth, *Z. Physik. Chem.*, **B20**, 333 (1933).

(12) This structure assignment is based on several facts: (1) all three possible hexanoylhexahydroperylenes were isolated; (2) one of the minor ketones (*ca.* 25%) was dehydrogenated with reduction of the carbonyl group to known 3-*n*-hexylperylene and therefore possesses the structure 4-hexanoylhexahydroperylene; (3) assignment of structure to the major ketone product is confined to a choice between C-5 and C-6 in HHP; (4) the behavior of the major ketone product on treatment with palladium on charcoal paralleled that of 5-acetyl-HHP. With either ketone, the hexahydroperylene system was smoothly oxidized to a simple substituted perylene. In sharp contrast, attempted dehydrogenation of 6-acetyl-HHP (**8**) gave a cyclic aryl ether, for



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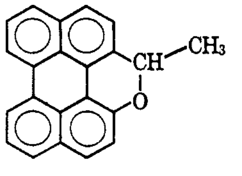

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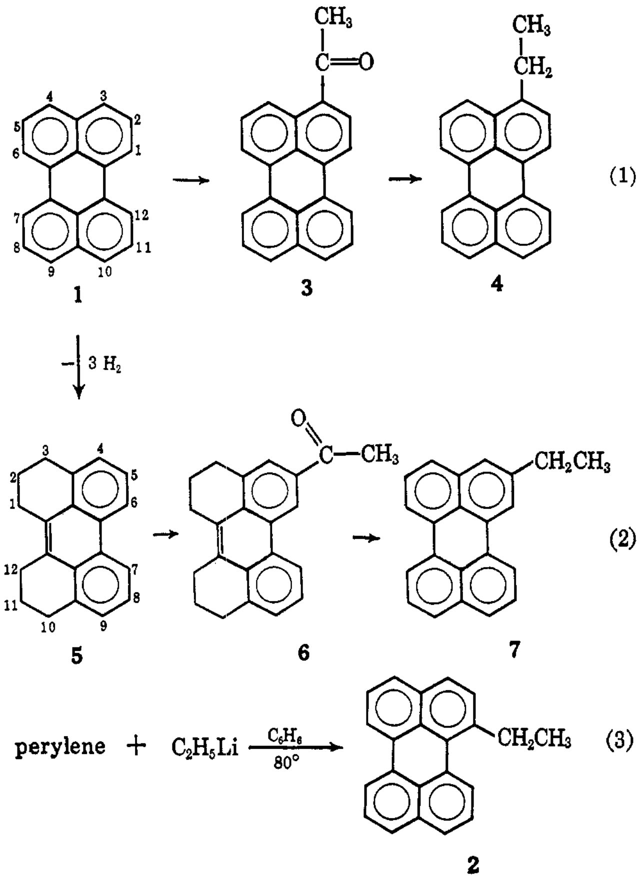
which structure **9** is proposed. These results provide compelling evidence that the major ketone product is 5-hexanoyl-HHP rather than the 6 isomer.

lithium and perylene in benzene[13] for 48 hr gave 1-ethylperylene needles (25%). The chemical, physical and spectral properties of this substance are analogous to those for the previously described 1-*n*-butylperylene homolog.[7] The syntheses of the isomeric ethylperylenes are summarized in Scheme II.

SCHEME II



The successful Friedel–Crafts acylations of **1** and **5** with acetyl and hexanoyl chloride demonstrate that eq 1 and 2 are general methods for securing C-3 and C-2 substituted perylenes in good yields. On the contrary, treatment of perylene with methyllithium–ether in boiling benzene afforded little methylation (0.1–2.0% of a crystalline methylperylene).[15] Invariably 90–95% of the starting perylene was recovered.

Catalysis of methylation with N,N,N′,N′-tetramethylethylene diamine[17] increases the yield of alkylation slightly to 10%.[18]

Proton magnetic resonance spectra obtained on the isomeric ethylperylenes show the methyl triplet and methylene quartet characteristic of the ethyl group. A complex aromatic multiplet, having an ABX type of spectrum similar to that reported for the parent hydrocarbon,[19] is present. The signals at lowest field from cyclohexane in 40-Mc spectra have been assigned to the C-1, -6, -7, and -12 protons in perylene.[20] This assignment is based upon a comparison of the nmr spectra for perylene, phenanthrene, and 4-methylphenanthrene and structurally similar polynuclear aromatic hydrocarbons.[21]

In the proton nmr spectra for the ethylperylenes at 60 Mc with internal tetramethylsilane (TMS), the signals arising from the aromatic protons are cleanly separated into two groups. The A–B absorptions occur at higher fields (τ 2.2–2.9) and are of varying intensities and complexities. The X-type proton absorptions occur between τ 1.8 and 2.0 and are much simpler.

The integration curve for 1-ethylperylene shows only three protons at lowest field from TMS in the form of two distinct doublets at τ 1.87 and 1.99; 2-ethylperylene's spectrum integrates properly for four aromatic protons of the X type (in the form of a multiplet, having considerable fine structure, centered at τ 1.97 with a doublet at τ 2.11). Thus the earlier assignment of proton resonance signals at lowest field to the aromatic protons of carbon atoms 1, 6, 7, and 12 in perylene agrees with the structural assignments which are based on isomer number, method of synthesis, and alternate syntheses of 3-*n*-hexylperylene. The chemical shifts from TMS for the isomeric ethylperylenes are given in Table I.

TABLE I

CHEMICAL SHIFTS[a] FROM TETRAMETHYLSILANE FOR ETHYLPERYLENES IN DEUTERIOCHLOROFORM

	1-Ethylperylene	2-Ethylperylene	3-Ethylperylene
Methyl group triplet	8.56	8.70	8.62
Methylene quartet	6.86	7.28	6.96
Aromatic multiplet			
(A–B)	2.26–2.83[b]	2.32–2.85[c]	2.36–2.78[d]
(X)	1.86–2.00	1.90–2.12	1.79–1.98

[a] Given as τ values. [b] Twenty lines. [c] Sixteen lines. [d] Twenty-two lines.

The infrared spectra of the isomeric ethylperylenes exhibit distinct patterns in the 11–15-μ region. The data, which are characteristic for each position in perylene, are summarized in Table II.

Data for some of the other perylene derivatives described above have the same characteristic absorptions from 11 to 15 μ as were found for the ethylperylenes. See Table III.

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(13) In tetrahydrofuran alkylation of perylene with butyllithium is extremely facile. At temperatures of −30°, equimolar amounts of **1** and *n*-butyllithium furnished a 44% yield of 1-butylperylenes.[14]

(14) Unpublished studies of H. E. Zieger and Mrs. J. E. (Rosenkranz) Selwyn.[7]

(15) We are continuing to investigate the methylation of perylene with methyllithium because mp 119–121° of the methylperylene we have isolated does not agree with the literature melting points[16] for any of the isomeric methylperylenes. An H^1 nmr spectrum, C and H analyses, and an ultraviolet spectrum show the new hydrocarbon to be 1-methylperylene. The mass spectrum has a parent peak at mass 266 and shows impurities at masses 252 (perylene), 268 (possibly methyldihydroperylene), and 280 (dimethylperylene). Thanks are due Dr. T. F. Yen at the Mellon Institute for securing this spectrum on the MS-9 high-resolution mass spectrometer.

(16) A. D. Campbell, R. A. Elder, and G. W. Emerson, *J. Chem. Soc.*, 3526 (1959).

(17) G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964); C. G. Screttas and J. F. Eastham, *J. Am. Chem. Soc.*, **87**, 3276 (1965); A. W. Langer, Jr., *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965).

(18) Current studies at short reaction times by E. Laski, National Science Foundation Undergraduate Research Participant, have given a crystalline methyldihydroperylene which on dehydrogenation provides 1-methylperylene.

(19) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

(20) H. J. Bernstein and W. G. Schneider, *ibid.*, **24**, 468 (1956).

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 250–253.

TABLE II

CHARACTERISTIC INFRARED ABSORPTIONS[a] OF THE ETHYLPERYLENES

1-Ethylperylene	2-Ethylperylene	3-Ethylperylene
...	11.2 w	...
...	11.60 s	...
12.13 vs	12.00 vs	12.05 s
	12.4 w	
12.5 m	12.45 vs	12.37 vs
13.03 vs	13.0 vs	13.11 vs
13.24 s	13.3 m	13.35 s
14.03 w	...	...
14.67 m	14.7 vw	...

[a] Values are given as microns. w = weak, m = medium, s = strong, vs = very strong. All spectra were obtained in KBr pellets on a Perkin-Elmer Model 21 spectrophotometer.

TABLE III

CHARACTERISTIC INFRARED ABSORPTIONS[a] OF THE C-2 AND C-3 CARBOXY- AND HEXANOYLPERYLENES

2-Hexanoylperylene	Perylene-2-carboxylic acid
...	11.1 m
11.98 vs	11.8 m
12.30 w	12.3 vs
12.50 s	12.8 vs
13.03 vs	...
13.40 vw	...
13.78 m	13.9 m
3-Hexanoylperylene	Perylene-3-carboxylic acid
12.18 sh	11.91 w
12.37 vs	12.32 vs
13.00 vs	13.08 vs
13.09 sh	13.15 sh
...	13.70 m

[a] Values are given as microns.

Experimental Section

3-Acetylperylene.—Perylene[22] (6.27 g, 0.0249 mole), aluminum chloride (4.47 g, 0.0335 mole, Matheson Coleman and Bell), and dry chlorobenzene (1.20 l.) were treated dropwise at 0° with acetyl chloride (2.05 g, 0.0261 mole in 300 ml of dry chlorobenzene) during 1.7 hr. The temperature was maintained at 0° for an additional 1.5 hr before warming to 23° during 14 hr. The reaction mass was hydrolyzed on cracked ice, salts were dissolved with HCl (50 ml), and chlorobenzene was removed by steam distillation. The solid which remained was partially dissolved in 2.2 l. of boiling carbon tetrachloride. The residue weighed 1.06 g (14.5%).

The carbon tetrachloride solution was dried over calcium chloride and was purified by chromatography over 165 g of activated alumina. The products isolated were 1.66 g of perylene (26.5%, mp 277-280°) and 3.96 g of 3-acetylperylene (54.1% mp 245.5-247.0°).

Anal. Calcd for $C_{22}H_{14}O$: C, 89.77; H, 4.79. Found: C, 89.63; H, 4.85.

3-Hexanoylperylene.—Perylene (6.30 g, 0.025 mole, Rutgerswerke Co.[24]), aluminum chloride (4.76 g, 0.0356 mole), and fractionally distilled hexanoyl chloride (3.88 g, 0.0288 moles) were mixed in dry chlorobenzene under conditions as similar to those described for 3-acetylperylene as possible. After purification by chromatography (CCl_4), 1.20 g of perylene (19.0%), 5.49 g of 3-hexanoylperylene (a, 62.7%, mp 181.6-182.2°), and 1.30 g of dihexanoylperylenes (b, 11.6%, mp 240-248°) were isolated.

Anal. Calcd for $C_{26}H_{22}O$ (a): C, 89.11; H, 6.33. Found: C, 89.32; H, 6.37.

Anal. Calcd for $C_{32}H_{32}O_2$ (b): C, 85.71; H, 7.14. Found: C, 86.10; H, 7.26.

Perylene-3-carboxylic Acid.—Perylene-3-carboxylic acid was prepared by the partial decarboxylation[25a] of 3,4,9,10-perylenetetracarboxylic 3,4:9,10-dianhydride[25c] (52.5 g, 0.134 mole) with potassium hydroxide (120 g, 2.14 moles) and distilled water (880 g) in a stainless steel liner for a rocking-shaker-type autoclave.

The autoclave was shaken for 40.5 hr at 210 ± 2° at an autogenous pressure of 175 psi. After cooling, crude potassium perylene-3-carboxylate (33.0 g, 74%) was separated. Soxhlet extraction of this salt with chloroform removed some perylene (1.8 g, mp 278-280°). Digestion of the salt residue with water (2.0 l.) containing HCl (50 ml) afforded crude perylene-3-carboxylic acid (mp 325-328°). Recrystallization from nitrobenzene-dimethylformamide (700-50 ml) gave 18.0 g of impure perylene-3-carboxylic acid (45.3%, mp 333-335°). Conversion of this crude acid (13.1 g) to its methyl ester (12.46 g, 90.7%, mp 208-214°) was followed by purification by chromatography over alumina dust (200 g, Alcoa F-20) which had been deactivated with 3.0 ml of 10% acetic acid in 2 l. of hexane. The products isolated were perylene (0.05 g, mp 276-281°) and methylperylene-3-carboxylate (8.24 g, mp 210-211°, lit.[26] mp 198-200°).

The saponification equivalent of the purified ester was determined. Calcd for $C_{22}H_{14}O_2$: 310. Found: 315. Perylene-3-carboxylic acid was recovered by acidifying the salt suspension obtained from the saponification of 2.78 g of ester. The acid was filtered, washed with anhydrous ether, and dried in a vacuum desiccator (2.54 g, 96%, mp 334.8-335.0°; lit.[27] mp 330, 334°).

Perylene-3-carbonyl Chloride.—Perylene-3-carboxylic acid (1.06 g, 0.00358 mole) was mixed with thionyl chloride (80 ml, Eastman White Label) and anhydrous benzene (20 ml). The solution was refluxed for 4.2 hr. Excess thionyl chloride was removed at reduced pressure and crude solids were recrystallized from benzene-hexane (1:1) to yield 1.08 g of perylene-3-carbonyl chloride (96.4%, mp 182-190°). The purest crystals had mp 181-183°. Infrared spectra indicated that trace amounts of unconverted acid were present.

3-Hexanoylperylene.—Dipentyl cadmium (0.0491 mole) was prepared using *n*-amyl bromide (12.0 ml, 0.0982 mole), magnesium (3.25 g, 0.134 g-atom), and cadmium chloride (11.10 g, 0.0606 mole, Fisher Scientific Co.) as described for isoamyl bromide.[28]

To the benzene solution of dipentyl cadmium was added a solution of perylene-3-carbonyl chloride (1.19 g, 0.0378 mole in 150 ml of dry benzene). The mixture was refluxed for 3.5 hr and hydrolyzed with ice. The organic phase was separated, dried over calcium chloride and purified by elution chromatography over activated alumina (50 g) to yield 0.73 g of 3-hexanoylperylene (55.3%, mp 180-182°). A mixture melting point with ketone obtained by Friedel-Crafts hexanoylation of perylene was undepressed. The infrared spectra obtained on these two samples were identical.

3-Ethylperylene.—3-Acetylperylene (0.96 g, 0.00326 mole), hydrazine hydrate (10.0 ml, 100% Mathieson Chemical Co.), potassium hydroxide (5.45 g, 0.0971 mole) and triethylene glycol (95 ml, Fisher Scientific, pre-purified) were mixed for Wolff-Kishner reduction by the Huang-Minlon method.[29]

After evolution of 110 ml of nitrogen gas and cooling, hydrolysis was accomplished on ice. The organic materials were extracted into chloroform. After drying ($CaCl_2$) and distillation of excess solvent, 0.83 g of crude 3-ethylperylene (91.2%, mp 160-163°) were deposited. Recrystallization from ethanol-acetone (10:1) gave 0.45 g of purified hydrocarbon, mp 163.8-164.6°. The ultraviolet spectrum is given in Table I in ref 7.

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[22] Perylene used in this work was prepared as described previously.[7] It had mp 282.5-283.5° (lit.[23] mp 273-274°) obtained on an Anschütz thermometer which had been calibrated against one provided by the National Bureau of Standards. A Nalge-Axelrod melting point apparatus was used.

[23] G. T. Morgan and J. G. Mitchell, *J. Chem. Soc.*, 536 (1934).

[24] Perylene purchased from Rutgerswerke Co. had mp 281-282° and was used directly without further purification.

[25] (a) Decarboxylation conditions for this system are well known: W. Neugebauer, German Patent 486,491 (1926);[25b] *Chem. Abstr.*, **24**, 1870 (1930). (b) "Elsevier's Encyclopedia of Organic Compounds, Series III, Carboisocyclic Condensed Compounds," Vol. 14, F. Radt, Ed., Elsevier Publishing Co., Amsterdam C, The Netherlands, 1951, p 734 S. (c) Available commercially from the Putnam Chemical Co., Beacon, N. Y.

[26] K. Koberle and O. Schlichting, German patent 703,500, (Feb 6, 1941); *Chem. Abstr.*, **36**, 781[2] (1942).

[27] Reference 4 gives mp 322-334°. Reference 25b, p 743 S, quotes ref 25a, mp 330°.

[28] J. Cason and F. S. Pout, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 601.

[29] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.13; H, 5.83.

3-*n*-Hexylperylene.—3-Hexanoylperylene (2.43 g, 0.00694 mole), hydrazine hydrate (5 ml, 100% Mathieson Chemical Co.), potassium hydroxide (5 g, 0.089 mole), and triethylene glycol (100 ml, Fisher Scientific pre-purified) were reduced by the Huang-Minlon modification of the Wolff–Kishner method as described for 3-ethylperylene.

Purification of the reaction product was accomplished by chromatography using activated alumina (20 g) to yield 2.09 g of 3-hexylperylene (89.7%, mp 141.8–142.6°).

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.55; H, 7.08.

1,2,3,10,11,12-Hexahydroperylene.—Perylene (50.40 g, 0.200 mole) was hydrogenated in a high-pressure apparatus supplied by the American Instrument Co., Silver Spring, Maryland. It was of the heated-autoclave, rocking-shaker type. The solvent was decalin (1.0 l.) and the catalyst was copper chromite (5.09 g of G-22, The Girdler Corp., Louisville, Kentucky) supported on finely powdered carbon. A stainless steel liner of about 2.5-l. volume was used.

After hydrogen absorption ceased, the catalyst was separated by hot filtration and was extracted with portions of hexane and benzene; the combined organic solutions were distilled. After cooling, 39.32 g of hexahydroperylene (76.20%, mp 190–193°; lit.[30] mp 189°), was isolated. After distillation of solvents an additional 6.19 g of hexahydroperylene (12.2%, mp 185–191°) was obtained.

A sample of hexahydroperylene (10 g) was purified by chromatography over alumina using hexane solvent. A trace of perhydroperylenes (0.10 g, mp 82–88°) was isolated and identified by its infrared spectrum. Purified 1,2,3,10,11,12-hexahydroperylene (8.61 g, mp 193.2–194.1°) was obtained.

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.06; H, 7.08.

None of the unknown isomeric 1,2,3,7,8,9-hexahydroperylene was isolated.

5- and 6-Acetyl-1,2,3,10,11,12-hexahydroperylene.—1,2,3,-10,11,12-Hexahydroperylene (32.11 g, 0.124 mole), aluminum chloride (20.46 g, 0.153 mole), and dry chlorobenzene (750 ml) at 0° were treated dropwise during 1.3 hr with acetyl chloride (9.76 g, 0.124 mole) in 210 ml of dry chlorobenzene. The system was maintained at 0° for 2.5 hr and was warmed gradually to room temperature with stirring (16 hr).

After hydrolysis on ice and steam distillation of chlorobenzene, the product was dissolved in carbon tetrachloride (1.5 l.). Upon drying ($CaCl_2$) and distillation to 0.5-l. volume, 17.60 g (47.3%) of ketones were secured (mp 160–173° and mp 145–175°). Complete removal of the carbon tetrachloride afforded 22.90 g of an oil.

Partial purification of the solid ketones was obtained by chromatography over activated alumina (180 g of Alcoa dust, Grade F-20). Crude 5-acetyl-1,2,3,10,11,12-hexahydroperylene (14.31 g, 38.5%, mp 184–194°) was secured. Recrystallizations from ethanol-acetone or cyclohexane carbon tetrachloride mixtures gave purified 5-acetylhexahydroperylene (mp 192.5–194.0°).

Chromatography of the oil (as above) in benzene–hexane (70:30 ml) afforded additional 5-acetylhexahydroperylene (9.57 g, 25.8%) together with 6-acetylhexahydroperylene (7.03 g, 18.8%, mp 130–138°). Recrystallizations from ethanol-acetone (10:1) gave purified 6-acetyl-1,2,3,10,11,12-hexahydroperylene, mp 138.0–138.5°.

Anal. Calcd for $C_{22}H_{20}O$; C, 88.00; H, 6.67. Found for 194° isomer: C, 87.87; H, 6.86. Found for 138° isomer: C, 88.24; H, 6.83.

4- and 5-Hexanoyl-1,2,3,10,11,12-hexahydroperylenes.—1,2,3,10,11,12-Hexahydroperylene (51.9 g, 0.201 mole), aluminum chloride (35.3 g, 0.265 mole), and dry chlorobenzene (1.50 l.) at 0° were treated dropwise with hexanoyl chloride (29.11 g, 0.216 mole) during 3.0 hr. After warming to 23° during 4.5 hr, hydrolysis with HCl-ice and steam distillation of chlorobenzene, the oil was dissolved in hexane (4.0 l.). Upon chilling at −15°, 43.5 g of hexanoylhexahydroperylenes (60.8%, mp 100–106°) crystallized. A second crop (14.2 g, 19.8%, mp 97–106°) was obtained. After chromatography over alumina using hexane solvent purified 5-hexanoyl-1,2,3,10,11,12-hexahydroperylene (37.56 g, 52.5%, mp 108.5°–109.5°) was secured.

Anal. Calcd for $C_{26}H_{28}O$: C, 87.59; H, 7.92, 87.87, 7.98. The 2,4-dinitrophenylhydrazone had mp 255.5–256.5°.

Chromatographic fractions which afforded uncrystallized oils were combined with the hexane mother liquor, which was chromatographed to yield 17.9 g (25%) of impure 4-hexanoyl-1,2,3,-10,11,12-hexahydroperylene (mp 140–160°). Three recrystallizations from hexane afforded purified ketone, mp 164.0–166.0°. This ketone was dehydrogenated over Pd-C (5% Baker and Co., Inc., Catalysts) at 290° with reduction of the carbonyl group to 3-*n*-hexylperylene. A mixture melting point with an authentic sample was undepressed. The infrared spectrum was identical with that of 3-*n*-hexylperylene obtained from 3-*n*-hexanoylperylene.

Crude hexanoylhexahydroperylenes (5.53 g) from several runs were combined and purified by chromatography over activated alumina using hexane. Oils were obtained which upon crystallization using several drops of acetone gave two ketones, 5-hexanoylhexahydroperylene (mp 107.5–108.5°) and 6-hexanoylhexahydroperylene (mp 98.9–99.6°). A mixture melting point of 6- and 4-hexanoylhexahydroperylene was depressed (85–98°). Similarly a mixture melting point of 6- and 5-hexanoylhexahydroperylene was depressed (86.5–95°). Four analyses were obtained on the 6-hexanoyl-HHP isomer.[31]

Anal. Calcd for $C_{26}H_{28}O$: C, 87.59; H, 7.92. Found: C, 89.46, 88.10, 87.27, 86.79; H, 8.10, 8.11, 7.86, 7.68.

2-Ethylperylene.—In a test tube (15 × 3 cm) equipped with a glass stirrer were placed 5-acetyl-1,2,3,10,11,12-hexahydroperylene (1.36 g, 0.00453 mole) and 5% palladium on powdered charcoal (0.49 g, Baker and Co., Inc., Catalysts). The solids were stirred with heating at 290 + 10° for 9.75 hr.

After cooling the products were extracted from the catalyst with chloroform and with acetone. The product crystallized from ethanol–acetone (10:1) and had mp 110–113°. Recrystallization from ethanol gave 0.81 g of 2-ethylperylene (63.8%, mp 112.0–113.3°). Mixture melting points with 3-ethylperylene and 1-ethylperylene were depressed. See Table II in ref 7 for ultraviolet results.

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.38; H, 5.54.

2-Hexanoylperylene.—5-Hexanoyl-1,2,3,10,11,12-hexahydroperylene (0.70 g, 0.0196 mole) and 0.23 g of 20% palladium suspended on carbon catalyst were placed in a flask with a thermometer. The temperature was elevated to 229° and maintained for 23 min and the flask was cooled to room temperature. Organic products were extracted with carbon tetrachloride. After filtration and distillation, the hot carbon tetrachloride solution (30 ml) was diluted (1:1) with warm 95% ethanol. On cooling 0.26 g of 2-hexanoylperylene (38.2%, mp 116–119°) was secured. Crystallization of the material remaining in solution afforded 0.43 g of the starting 5-hexanoylhexahydroperylene (61%).

Purification of the crude 2-hexanoylperylene by two recrystallizations from ethanol–acetone (1:1) gave an analytical sample (mp 123.3–124.4°).

Anal. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 89.30; H, 6.50.

1,2,3,10,11,12-Hexahydroperylene-5-carboxylic Acid.—5-Acetylhexahydroperylene (2.30 g, 0.00767 mole) was dissolved in 200 ml of dioxane and was treated with 50 ml of 0.10 *N* iodine–potassium iodide solution and 40 ml of 10% sodium hydroxide. The solution was maintained at 60° for 2 hr. Ice (250 g) was added and unreacted ketone precipitated (1.12 g, 48.7%).

The aqueous phase was extracted with ether (3 × 100 ml) and was acidified to yield a white precipitate (0.98 g, 42.4%, mp 309–312°). Recrystallization of this acid from acetone gave purified hexahydroperylene-5-carboxylic acid, mp 311–312°. Sublimation furnished an analytical sample, mp 312°.

Anal. Calcd for $C_{21}H_{13}O_2$; C, 83.42; H, 6.00; neut equiv, 302.4. Found: C, 83.06, H, 5.99; neut equiv, 301.9.

Perylene-2-carboxylic Acid.—Hexahydroperylene-5-carboxylic acid (0.70 g, 0.00232 mole) and 5% palladium suspended on carbon (0.46 g) were heated in a test tube with stirring for 2.3 hr at 290–325°. The reaction products began subliming away from the catalyst. Perylene (0.38 g, 65%) and a mixture

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[30] A. Zinke and N. Schniderschitsch, *Monatsh.*, **51**, 280 (1929); see ref 10a.

[31] Microanalyses reported in this work were duplicates done by A. Bernhardt, Max Planck Institute, Mülheim (Ruhr), Germany. The analyst reported difficulty in obtaining precision on this compound. He suggested that the compound undergoes autooxidation–reduction.

of perylene and perylene-2-carboxylic acid were isolated (0.06 g, 8.8%, mp 265–275° and 330–333°).

Extraction of the catalyst with ethanolic potassium hydroxide was followed by acidification of the filtered solution. After filtration and drying perylene-2-carboxylic acid was isolated (0.0398 g, 5.80%, mp 341.5–342.0°). A mixture melting point with perylene-3-carboxylic acid was depressed (313–320°).

Anal. Calcd for $C_{21}H_{12}O_2$: C, 85.12; H, 4.08. Found: C, 85.08; H, 4.42.

Attempted Dehydrogenation of 6-Acetyl-1,2,3,10,11,12-hexahydroperylene.—6-Acetyl-1,2,3,10,11,12-hexahydroperylene (2.04 g, 0.00680 mole) and 5% palladium suspended on carbon (0.91 g) were heated at 242–285° for 0.5 hr. After cooling, extraction with chloroform and crystallization from ethanol, 0.32 g of a material (mp 116.8–120.0°) having an infrared spectrum (KBr) with a strong absorption at 1232 cm^{-1}, which suggests a structure of 1-ethylperylene-β,12-cyclo oxide, **9**, was isolated.

Anal. Calcd for $C_{22}H_{14}O$; C, 89.77; H, 4.79. Found: C, 90.04; H, 5.08.

1-Ethylperylene.[32]—Ethyllithium (0.053 mole, 1.78 *N*, Lithium Corp. of America) in benzene was added dropwise during 0.50 hr to a 0.033 *M* benzene solution of perylene (12.60 g, 0.050 mole) under a dry argon atmosphere with stirring. After 48 hr at 80°, the reaction mass was hydrolyzed with water (3.0 ml). Solvents were distilled and the residue was dissolved in hexane (550 ml). Chromatography of the hexane solution over alumina (Alcoa Activated Dust, Grade F-20) yielded 1-ethylperylene (3.4 g, 24%, mp 78–84°) in the early eluate fractions (eluent, hexane) together with uncrystallizable oils in some fractions.

Recrystallization of 1-ethylperylene from 95% ethanol furnished yellow needles, mp 84–85°.

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.26; H, 5.80.

The 1,3,5-trinitrobenzene derivative had mp 199–200°; ultraviolet, λ_{max} mμ (log ϵ), 251 (4.47), 257.5 (4.71), 265 infl (4.32), 383.5 (4.03), 403.5 (4.35), 427 (4.42).

A benzene solution of commercial ethyllithium (Lithium Corp.) was refluxed for 24 hr, was hydrolyzed with water, and shown to contain less than 0.07% ethylbenzene (if any) by gas chromatography. Control solutions were analyzed easily in the range 0.07–0.7% ethylbenzene.

1-*n*-Butylperylene.—Freshly prepared 0.42 *N* *n*-butyllithium[33] (58.8 ml, 0.025 mole) in diethyl ether was added to a 0.025 *M* tetrahydrofuran solution of perylene (6.30 g, 0.025 mole) under a dry nitrogen atmosphere at −30 ± 2.5° during 1.0 hr. After 1.5 hr from the start of the organolithium addition, the reaction mass was added jetwise onto Dry Ice. Ether and tetrahydrofuran were distilled and the dry residue was extracted with boiling hexane (100 ml, four times). After crystallization of small amounts of perylene, the hexane extracts (50 ml) were chilled to −30°. An oil separated and the hexane solution was decanted. The oil coagulated (0.63 g, 8.2%, mp 61–64°) furnishing 1-*n*-butylperylene. Chilling of the hexane solution at −78° afforded 1.6 g of additional crystalline 1-butylperylene (20.8%, mp 60–67°).[34] After chromatography of the hexane solution, additional purified 1-butylperylene (1.2 g, 14%, mp 70.0–70.5° (uncor) lit. mp 66.5–67.0°) was secured. The salts were not investigated.

Nmr Data.—Pmr spectra were obtained on the isomeric ethylperylenes in $CDCl_3$ at 60 Mc with internal tetramethylsilane. Integration curves were secured for 1-ethyl- and 2-ethylperylenes; 3-ethylperylene was not soluble enough to give an integration curve. The intensities found for the methyl-, methylene-, and aromatic protons are shown in Table IV.

TABLE IV

	1-Ethyl-perylene, 8.5% by wt	Theory, %	2-Ethyl-perylene, 9.1% by wt
Methyl	5.31	5.33	5.71
Methylene	8.10	8.00	8.03
Aromatic	1.45	1.45	1.43
AB type	1.29	1.38	
AB type		1.57	1.57
X type	4.50	3.67	
X type		2.75	2.45

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[32] This synthesis was run by Miss E. Ellis, National Science Foundation Undergraduate Research Participant during 1964. 1-Ethylperylene was also prepared using ethyllithium prepared from lithium and ethylchloride.

[33] R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

[34] Isolation of 1-*n*-butylperylene by fractional crystallization from hexane indicates that purification by chromatography over alumina is not essential to securing 1-butylperylene.

Oxidation Reactions of Hexaphenylditin

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The tin–tin bond of hexaphenylditin is cleaved by a variety of common oxidants to give the corresponding triphenyltin compounds. The oxidation mechanism in the reaction of hexaphenylditin with sodium methoxide and air in tetrahydrofuran was investigated. In the presence of ethyl bromide, the oxidation yielded ethyltriphenyltin along with the usual products. The results are accounted for by assuming the existence of free triphenyltin radicals.

The results of a previous investigation[1] of the oxidation addition reactions of diphenyltin were found to be in accord with a reaction mechanism which involves the formation of a reactive triphenyltin radical intermediate.

It has been shown[2,3] that hexaphenyldisilane does not dissociate into triphenylsilyl radicals. However, the bond energy of the Sn–Sn bond is much lower than that of either the C–C or the Si–Si bond.[4] Those compounds which contain a Sn–Sn bond are quite reactive and are readily cleaved to form monotin compounds. In view of this lower bond energy hexaphenylditin (I) might be expected to react by dissociation into triphenyltin radicals and if this does occur it should be possible to trap these radicals and add further credence as to their existence.

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[1] W. L. Lehn and Tsu Tzu Tsai, unpublished results.

[2] H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951).

[3] H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

[4] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Text," Interscience Publishers, Inc., New York, N. Y., 1962, p 348.