290, and the minimum at 317–318 mμ (log ε 3.82–3.91) corresponds to that of psoralene. A very weak band at 328–330 mμ is also present which corresponds to the similar band of psoralene in this region.

The spectra of 2,3-dihydropsoralenes present very interesting features. Reduction of the furano ring caused the appearance of a band at 226 mμ (log ε 4.08–4.20). This has been considered to be due to the formation of a saturated ether which causes a bathochromic effect, offsetting the effect of the loss of conjugation.[9] The minimum at 221 and maximum at 245 mμ of psoralene is shifted to 253 and 256 mμ (log ε 3.41–3.60), resulting in a very weak band. The very sharp minimum at 265 ± 1 mμ (log ε 3.31–3.32) is characteristic for this group of compounds also. A very small band at 295 ± 1 mμ (log ε 3.75–3.80) is present and the maximum at 332 mμ (log ε 4.22–4.30) though broad is very characteristic.

In case of 5-phenyl-6-alkyl derivatives of dihydropsoralene, the characteristic minimum at 265 is shifted to 277 mμ (log ε 3.37–3.55), whereas in case of 5-phenyl dihydropsoralene, unsubstituted at the 6-position, the minimum occurs at 292 mμ (log ε 3.61). A broad band at above 335 mμ is present in all the three compounds.

Acknowledgment.—The authors are grateful to Mr. P. Bagchi, Director of Research, East India Pharmaceutical Works Ltd., Calcutta, for his kind interest and valuable suggestions, and to Mrs. C. Dutta of Indian Association for the Cultivation of Science, Calcutta, for the analyses.

(9) M. E. Brokke and B. E. Christensen, *J. Org. Chem.*, **23**, 590 (1958).

Alkylation and Metalation of Perylene with n-Butyllithium. 1-n-Butylperylene

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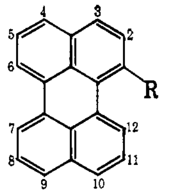
Recently Dixon and Fishman reported that aromatic hydrocarbons undergo alkylation with alkyllithium reagents to form mono- and dialkylated arenes in decalin at elevated temperatures.[2] During the course of metalation studies[3] on perylene (Ia) with n-butyllithium, at room temperature, we observed the alkylation reaction. One of the hydrocarbons which was isolated is thought to be 1-n-butylperylene and constitutes the first reported substitution of perylene at a position other than position three.

Two monosubstituted n-butylperylenes were isolated after column chromatography over alumina. One of these isomers (m.p. 138–139°) has an infrared spectrum which is difficult to distinguish from the spectrum for the known 3-n-hexylperylene.[4,5] The ultraviolet spectrum of this material compares favorably with the spectrum for the known 3-alkylperylenes[6,7] listed in Table I despite the fact that it was isolated in small amount and contained a difficult-to-remove impurity.



Ia, R = H
b, R = n-C_4H_9 –

The other n-butylperylene isomer (13.2%, m.p. 66.5–67.0°) has been assigned the structure 1-n-butylperylene (Ib) because its infrared spectrum differs from the spectra of the presumed 2-ethyl- and 2-n-hexylperylene in the region of 10–15 μ.[8] Furthermore, comparison of the n.m.r. spectrum of this butylperylene isomer with the spectrum of 3-n-hexylperylene shows an appreciable lower field chemical shift of 0.2 p.p.m. for the α-methylene signals.[9] Interestingly, the difference in chemical shift is greater (0.37 p.p.m.) for a comparison of 1-n-butylperylene and the presumed 2-ethyl- and 2-n-hexylperylene. This deshielding suggests that the n-butyl group is not at the 3-position and is predicted for the 1-position because of the increased ring-current effect expected for this position.

The ultraviolet spectrum of the new hydrocarbon bears a closer resemblance to the reported spectrum for 1-methylperylene[7] than for the spectrum of the presumed 2-ethylperylene (see Table II).

The n.m.r. spectrum[9] of 1-n-butylperylene exhibits proton signals: (1) at 0.9 and 1.0 p.p.m. from internal tetramethylsilane having an intensity ratio of 1:2.96 (theoretical = 1:2.86); (2) at 2.98 p.p.m. (center of a triplet), intensity ratio of 1:9.9 (theoretical = 1:10);

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(1) National Science Foundation Undergraduate Research Participant, spring semester and summer, 1963.

(2) J. A. Dixon and D. Fishman (a) *J. Am. Chem. Soc.*, **85**, 1356 (1963); (b) Abstracts of Papers, Division of Organic Chemistry, 145th National Meeting of the American Chemical Society, Sept. 1963, paper no. 101, p. 54Q.

(3) The solvent was ether-tetrahydrofuran and reaction conditions were chosen to approximate those found to be optimum for metalation in the naphthalene series: H. Gilman and S. Gray, *J. Org. Chem.*, **23**, 1476 (1958).

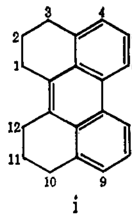
(4) 3-n-Hexylperylene (m.p. 141.8–142.6°) was prepared by Wolf-Kishner reduction of 3-n-hexanoylperylene. This ketone was secured by alternate syntheses: (a) Friedel-Crafts reaction of I and hexanoyl chloride (62.7%) and (b) the reaction of perylene-3-carbonyl chloride and di-n-pentylcadmium (55%).

(5) Details of this synthesis form a portion of the Ph.D. Thesis of H. E. Zieger, The Pennsylvania State University, Jan., 1961; *Dissertation Abstr.*, **22**(1) (1961).

(6) Ethylperylene was prepared from Ia by Friedel-Crafts acetylation (54%) and Wolf-Kishner reduction (95%).[5] The ultraviolet spectrum was obtained in cyclohexane.

(7) For 3-methylperylene see A. D. Campbell, R. S. Elder, and C. W. Emerson, *J. Chem. Soc.*, 3526 (1959).

(8) Only three monosubstituted perylenes are possible and the assumption[5] that was made is that 1,2,3,10,11,12-hexahydroperylene (i) furnished predominantly 5-acylhexahydroperylenes (61–63%) in Friedel-Crafts acylation. Because perylene derivatives secured from these ketones differed from their known 3-position isomers, they had to be either 1- or 2-derivatives of Ia



i

(9) N.m.r. spectra were obtained in carbon tetrachloride at 60 Mc./sec. Data for 2-ethylperylene and 2-n-hexylperylene were secured at the Central Research Laboratory of The Socony Mobil Oil Co., Inc., Princeton, N. J., under operating conditions similar to those for 1-n-butylperylene. Because of its low solubility, the spectrum of 3-n-hexylperylene was obtained in carbon disulfide.

TABLE I

ULTRAVIOLET SPECTRA

3-Ethylperylene[a]		3-*n*-Butylperylene		3-Methylperylene[b]		3-*n*-Hexylperylene[c]	
λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε
441.8	4.56	442.5	4.83	440	4.53	440.8	4.54
436.3	4.50 (infl.)	437.0	4.73	...	...	...	...
413.8	4.44	413.0	4.58	412.5	4.39	413.8	4.42
392.2	4.07	392.0	4.08	391	4.02	392.0	4.06
		373.0 (infl.)	3.70	370 (infl.)	3.53	371.8	3.63
266.6	3.98	265.0	4.04	268 (infl.)	3.85	266.3	3.88
254.9	4.67	255.1	4.75	254	4.61	254.2	4.59
247.6	4.53	246.5	4.54	246.5	4.45	247.0	4.45
239.7	4.21	227.0	4.28	...	...	227.1	4.26

[a] See ref. 6. [b] See ref. 7. [c] This spectrum was obtained in 95% ethanol for purposes of comparison with the spectrum of 3-methylperylene.

TABLE II

ULTRAVIOLET SPECTRA[a]

2-Ethylperylene[b]		2-Methylperylene[c]		1-Methylperylene[c]		1-*n*-Butylperylene	
λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε
436.0	4.57	435	4.53	433.5	4.52	427.6	4.60
410.0	4.46	408	4.41	406	4.40	404.0	4.51
388.7	4.13	387	4.08	384	4.10	384.5	4.08
		370 (infl.)	3.90	367 (infl.)	3.70		
264.3	4.10	266 (infl.)	3.97	268 (infl.)	3.88	258.2	4.71
254.4	4.70	253	4.65	258	4.65	251.8	4.52
247.6	4.54	246.5	4.51	245	4.52	...	...
241.1	4.28	208	4.76	208	4.72	...	...

[a] Ethyl- and 1-*n*-butylperylene were taken in cyclohexane; methylperylenes, in 95% ethanol. [b] See ref. 8. [c] See ref. 7.

and (3) at 7.05 to 7.95 p.p.m. (complex aromatic multiplet), intensity ratio 1:1.78 (theoretical = 1:1.82).

Reports of monosubstitution on perylene are few and always refer to electrophilic attack at position three.[5,7,10] Alkylation of perylene with *n*-butyllithium constitutes the first substitution on the perylene ring at a position other than position three. The new hydrocarbon is easily soluble in most common organic solvents at 20°. If this solubility behavior is general for 1-position derivatives, it is not surprising that earlier workers[10] were unable to isolate the small amounts of 1-position substitution products which probably were formed. What is surprising, however, is the amount of alkylation at the hindered 1-position. Substitution at such hindered positions in polynuclear systems has not been reported previously.[11]

The prediction of approximately equal reactivity for positions 1 and 3 in perylene is based on calculated MO reactivity indices.[12] The experimental evidence for such a prediction has been discussed.[13]

Experimental

Melting points were taken on a Nalge–Axelrod apparatus and are corrected.

Perylene.[14]—Perylene was prepared by decarboxylation of 3,4,9,10-perylenetetracarboxylic 3,4:9,10-dianhydride[15] by the method of Neugebauer.[16] The yields of perylene (m.p. 282.5–283.5°) after recrystallization from chloroform ranged from 78–85%. Perylene obtained in this manner was identical in all of its physical properties with a sample obtained from di-β-naphthol[17] using the ring-closing method of Zinke.[18]

***n*-Butyllithium.**—A 0.96 *N* solution of *n*-butyllithium in diethyl ether was prepared using 0.44 g.-atom of lithium and 0.21 mole of *n*-butyl bromide as described by Gilman.[19] The solution was assayed by the Gilman–Haubein method using benzyl chloride.

1-*n*-Butylperylene.—Freshly prepared *n*-butyllithium solution (0.51 mole, 1.19 *N*) was added dropwise during 1 hr. to a 0.025 *M* tetrahydrofuran (THF)[20] solution of perylene (12.60 g., 0.050 mole) under a dry nitrogen atmosphere at 28° with magnetic stirring. Gases were evolved (120 ml.). After 16 hr. of stirring, the reaction mass was added jetwise onto Dry Ice and stirred. Ether and THF were removed by distillation and 14.8 g. of yellow brown solid (dried *in vacuo*) remained. Extraction of this solid with four 125-ml. portions of *n*-hexane left a residue of 7.7 g. (dried *in vacuo*.) The hexane was distilled until the volume became 325–350 ml. Upon cooling at 5°, 0.55 g. of perylene (4.4%) precipitated. Chromatography of the hexane solution over Alumina (250 g. of Alcoa activated, Grade F-20, was used without further activation) yielded 1-*n*-butylperylene (2.035 g., 13.2%, m.p. 66.5–67.0° in the early fractions, 64–65° in later fractions).

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54; mol. wt., 308. Found: C, 93.40; H, 6.71; mol. wt., 311 (cryoscopic in benzene).

The ultraviolet spectrum was obtained in cyclohexane (see Table II).

Later chromatography fractions furnished 0.04 g. of 3-*n*-butylperylene (m.p. 136.8, 138–139°), identified by comparison of its infrared spectrum with that for 3-*n*-hexylperylene and 3-ethylperylene.[5]

The residue (7.7 g.) was extracted with four 125-ml. portions of hot benzene leaving 3.0 g. of light yellow lithium perylene

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(10) (a) N. P. Buu Hoi and C. T. Long, *Rec. trav. chim.*, **75**, 1221 (1956); (b) M. J. S. Dewar and E. Warford, *J. Chem. Soc.*, 3570 (1956).

(11) L. F. Fieser and M. Fieser, "Topics in Organic Chemistry," Reinhold Publishing Co., New York, N. Y., 1963, Chapter 1; (b) M. S. Newman, *J. Am. Chem. Soc.*, **62**, 2295 (1940).

(12) J. Koutecky, R. Zahradnik, and J. Cizek, *Trans. Faraday Soc.*, **57**, 169 (1961); M. J. S. Dewar, *J. Am. Chem. Soc.*, **14**, 3357 (1952).

(13) A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 344.

(14) Perylene used in this work was generously supplied by Professor J. A. Dixon, The Pennsylvania State University.

(15) Decarboxylation conditions for this system are well known; K. Koberle and O. Schlichting, German Patent 703,500 (1941); *Chem. Abstr.*, **36**, 781^2 (1941); "Elsevier's Encyclopedia of Organic Compounds, Series III, Carboisocyclic Condensed Compounds," Vol. 14, F. Radt, Ed., 1951, p. 734 S.

(16) German Patent 486,491 (1926).

(17) R. Pummerer, E. Prell, and A. Rieche, *Ber.*, **59**, 2160 (1926).

(18) K. Brass and E. Tengler, *ibid.*, **64**, 1646 (1931); F. Hansgirg and A. Zinke, *Monatsh.*, **40**, 403 (1919).

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

(20) Matheson Coleman and Bell THF (b.p. 65.5–66.5°) was distilled first from sodium ribbon into a flask containing lithium aluminum hydride, then directly into the reaction flask containing perylene.

carboxylate salts (infrared spectrum, KBr) undissolved.[21] Impure perylene (1.4 g., 11.1%) crystallized from the benzene solution. Chromatography of this solution furnished additional perylene (1.1 g., 9%).

Acknowledgment.—We are indebted to Professor J. A. Dixon, Pennsylvania State University, for securing the n.m.r. spectra and for helpful discussions and encouragement. We are obliged to the City University of New York for a research grant permitting continuation of this investigation.

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(21) Investigation of the isomer composition of the methyl esters of the perylenecarboxylic acids by chromatography is in progress.

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p-Nitrobenzoic *t*-Butyl Thiolcarbonic Anhydride[1]

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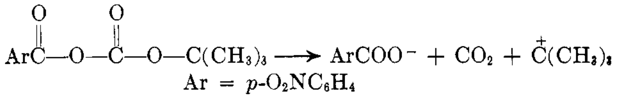
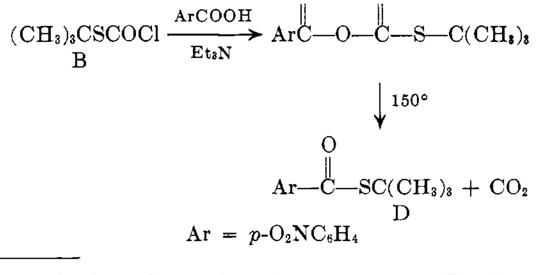
The products formed in the thermal decomposition of *p*-nitrobenzoic *t*-butyl carbonic anhydride[2] (A) indicate that it undergoes alkyl–oxygen cleavage, as shown, rather than the acyl–oxygen cleavage observed with mixed anhydrides with primary or secondary alkyl groups.[3] This note reports the preparation and properties of the sulfur analog of A.



$$\mathrm{Ar\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}C(CH_3)_3 \longrightarrow ArCOO^- + CO_2 + \overset{+}{C}(CH_3)_3}$$

$$\mathrm{Ar} = p\text{-}\mathrm{O_2NC_6H_4}$$

t-Butyl thiolchlorocarbonate (B) was prepared, apparently for the first time,[4] by the action of sodium hydride dispersion on *t*-butyl mercaptan in THF, followed by addition of phosgene in THF. *t*-Butyl thiolchlorocarbonate was distilled *in vacuo* and showed carbonyl absorption[5] at 1770 cm.$^{-1}$; it was converted in the usual way into the crystalline mixed anhydride C, m.p. 86.5–87°, which showed bands at 1730 and 1786 cm.$^{-1}$. The mixed anhydride C was converted by heating at 160° to the *p*-nitrothiolbenzoate D (identified by comparison with a synthetic sample) and carbon dioxide; no other products were observed.



$$\underset{\mathrm{B}}{\mathrm{(CH_3)_3CSCOCl}} \xrightarrow[\mathrm{Et_3N}]{\mathrm{ArCOOH}} \mathrm{Ar\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}S{-}C(CH_3)_3} \xrightarrow{150^\circ} \mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}SC(CH_3)_3} + \underset{\mathrm{D}}{\mathrm{CO_2}}$$

$$\mathrm{Ar} = p\text{-}\mathrm{O_2NC_6H_4}$$

The contrast between the behavior of the sulfur compound C and the oxygen analog A is therefore striking; the former gives no apparent alkyl–sulfur cleavage, and gives high yields of products formed by a single mode of decomposition. The oxygen analog A decomposes at a lower temperature and gives a complex mixture of products, some of which are a result of alkyl–oxygen cleavage.

This pair of sulfur–oxygen analogs illustrates the smaller tendency for alkyl–sulfur cleavage as compared to alkyl–oxygen cleavage, which has been observed in numerous other cases.[6]

Experimental

***t*-Butyl Thiolchlorocarbonate (B).**—*t*-Butyl mercaptan (45 g., 0.5 mole) in anhydrous tetrahydrofuran was added slowly with stirring to a slurry of sodium hydride dispersion[7] (50% in mineral oil; 25 g., 0.5 mole) in tetrahydrofuran and the mixture was refluxed with stirring under nitrogen for 2–4 hr. This suspension was then cooled and added with shaking to phosgene (50 g., 0.5 mole) contained in a flask equipped with stirrer and dry ice condenser and cooled in an ice–salt mixture. Air was carefully excluded during the addition to prevent oxidation of the mercaptide. After additional stirring for 2 hr. at room temperature, the mixture was centrifuged and filtered. The filtrate on distillation *in vacuo* yielded fractions boiling at 50–55° (13 mm.). On redistillation, the product boiling at 30–32° (1 mm.) was collected; this formed a thiocarbamate with aniline which had a melting point that was identical with the literature value[8] (147.5–148°).

Anal. Calcd. for C_5H_9ClOS: C, 39.36; H, 5.94; S, 21.02; Cl, 23.23. Found: C, 39.58; H, 6.18; S, 20.74; Cl, 23.05.

***p*-Nitrobenzoic *t*-Butyl Thiolcarbonic Anhydride (C).**—Dry ether (300 ml.) was chilled to −5° by an ice–salt bath, then *p*-nitrobenzoic acid (1.67 g., 0.01 mole) and *t*-butyl thiolchlorocarbonate (1.53 g., 0.01 mole) were added. The mixture was stirred and 1.01 g. (0.01 mole) of triethylamine in ether was added dropwise. The stirring was continued for 2 hr. more and the resulting mixture was filtered, washed with very dilute acid, with sodium bicarbonate solution and water, and was dried. The ether was evaporated at room temperature at reduced pressure leaving a material which was contaminated with *p*-nitrobenzoic acid; this was removed by extracting the material with carbon tetrachloride in the cold, leaving the mixed anhydride in 80–90% yield. The product was recrystallized twice or thrice from a mixture of carbon tetrachloride and petroleum ether, avoiding strong and prolonged heating. After three crystallizations, the pale yellow needles melted at 86.5–87°. The infrared spectrum contained peaks at 1730 and 1785 cm.$^{-1}$ which are characteristic of mixed carboxylic–carbonic anhydrides.[9] Ultraviolet absorption in cyclohexane showed $\lambda_{\max}$ 254 mμ (ϵ 26,900).

Anal. Calcd. for $C_{12}H_{13}NO_5S$: C, 50.86; H, 4.62; N, 4.94; S, 11.32. Found: C, 50.92; H, 4.58; N, 4.97; S, 11.24.

Decomposition of the Mixed Anhydride.—In a typical run designed to determine the yield of carbon dioxide, *p*-nitrobenzoic *t*-butyl thiolcarbonic anhydride (0.363 g., 0.00128 mole) was placed in a 10-ml. two-necked flask; through one neck a stream of prepurified nitrogen (free from oxygen and carbon dioxide) was led and the other neck carried an outlet tube and a condenser with an outlet tube. The outlet tube was connected to two microascarite tubes. The sample was heated at 160° for 2 hr. and 0.0595 g. of carbon dioxide was collected (106% of theory). The pot residue was recrystallized from ethanol–water, melted at 75.0°, and did not depress the melting point of an authentic sample of *t*-butyl *p*-nitrothiolbenzoate prepared as below. The infrared spectra of the two were identical.

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(1) Aided by Grant G-11240 from the National Science Foundation.

(2) C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, **29**, 1168 (1964).

(3) E. J. Longosz and D. S. Tarbell, *ibid.*, **26**, 2161 (1961); C. J. Michejda, D. S. Tarbell, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **84**, 4113 (1962).

(4) *t*-Butoxycarbonyl derivatives have been studied extensively by L. A. Carpino [*e.g.*, *ibid.*, **79**, 98 (1957); **82**, 2725 (1960)] and have been used as protecting groups in peptide syntheses.

(5) A. W. Baker and G. H. Harris [*ibid.*, **82**, 1923 (1960)] report that CH_3SCOCl absorbs at 1766 cm.$^{-1}$.

(6) P. N. Rylander and D. S. Tarbell, *ibid.*, **72**, 3021 (1950); B. K. Morse and D. S. Tarbell, *ibid.*, **74**, 416 (1952); D. S. Tarbell, and J. C. Petropoulos, *ibid.*, **74**, 244 (1952); L. A. Carpino, P. H. Terry, and P. J. Crowley, *J. Org. Chem.*, **26**, 4336 (1961); D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1 (1951).

(7) Obtained from the Metal Hydrides Corp.

(8) E. Dyer and J. F. Glenn, *J. Am. Chem. Soc.*, **79**, 366 (1957).

(9) D. S. Tarbell and N. L. Leister, *J. Org. Chem.*, **23**, 1149 (1958).