coholic potassium hydroxide, in accord with its bridgehead position. Nmr ($CDCl_3$) showed singlets at 0.99 and 2.16 ppm in a 9:2 ratio.

Use of pivaloyl bromide and stannic bromide gave the bromo analog in 28% yield. With chloropivaloyl chloride and stannic chloride a 0.5% yield of 7-chloro-1,3,5-tris(2-chloro-1,1-dimethylethyl)-2,4,9-trioxaadamantane was obtained.

Experimental Section

7-Chloro-1,3,5-tri-*tert*-butyl-2,4,9-trioxaadamantane.—Pivaloyl chloride (80 g, 0.66 mol) was placed in a 500-ml, three-necked flask equipped with magnetic stirrer, Dry Ice condenser, thermometer, and inlet tube. The flask was cooled to −30° and 50 g (0.9 mol) of liquid isobutylene was introduced. The inlet tube was replaced with a small dropping funnel and anhydrous stannic chloride (7 ml, 16 g, 0.06 mol) was added dropwise during 45 min while the temperature was maintained at *ca.* −15° by cooling with Dry Ice–acetone. The cooling bath was removed and the mixture was allowed to stand for 1 hr. The crystals of the trioxaadamantane were filtered off and rinsed with methanol. The original filtrate was kept separate from the methanol rinse. The yield at this point was 24 g (32%): mp 161–162° after recrystallization from acetone; ir 2976, 2882 (CH), 1389, 1359 (gem CH_3 groups), 1175–1050 cm^{-1} (multiple strong bands for C–O–C–O–C), no evidence of C=O, C=C, OH.

Anal. Calcd for $C_{19}H_{33}ClO_3$: C, 66.16; H, 9.64; Cl, 10.28; mol wt, 345. Found: C, 66.21; H, 9.78; Cl, 10.14; mol wt, 339 (cryoscopic in benzene).

After standing for a day, the original filtrate from the crystals was distilled to give 21.3 g (23%) of 2,2,5-trimethyl-4-hexen-3-one:[3] bp 67–68° (24 mm); $n^{25}D$ 1.4437; nmr (neat) 0.75 [s, $(CH_3)_3C$], 1.52 and 1.72 [unsharp doublets, $=C(CH_3)_2$], 5.98 ppm (broad peak, =CH). The pot residue yielded 4.7 g (6%) more of the trioxaadamantane. In a run in which the liquid product was distilled immediately, HCl had not split out and 5-chloro-2,2,5-trimethyl-3-hexanone, $(CH_3)_3CCOCH_2CCl(CH_3)_2$, distilled out: bp 71–72° (12 mm); $n^{25}D$ 1.4367; nmr (neat) 0.97 [s, $C(CH_3)_3$], 1.53 [s, $ClC(CH_3)_2$], 2.92 ppm (s, CH_2), no =CH peak. On standing overnight, the chloro ketone turned dark and evolved HCl. External tetramethylsilane was used as nmr reference for all compounds.

The reaction between pivaloyl chloride and isobutylene was tried in the stoichiometric ratio of 3:1, without solvent and with hexane as a solvent, but the yields of the trioxaadamantane filtered off were only 11 and 9%, respectively. When a mole ratio of 1:1 was used, without solvent, the yield filtered off was 35%.

7-Bromo-1,3,5-tri-*tert*-butyl-2,4,9-trioxaadamantane.—The reaction was carried out as for the chloro compound using 25 g (0.15 mol) of pivaloyl bromide,[7] 8 g (0.14 mol) of isobutylene, and 4 g (0.009 mol) of stannic bromide.[8] The mixture did not become noticeably exothermic at −15°, but when the cooling bath was removed the temperature eventually rose to 33° and crystals separated. The cooled mixture was filtered and the crystals were rinsed with methanol to give 5.4 g (28%) of the trioxaadamantane. Recrystallization from acetone left 4.6 g: mp 166°; ir 2967, 2882 (CH), 1393, 1376 (*gem*-CH_3 groups), 1175–1050 cm^{-1} (multiple bands for C–O–C–O–C); nmr ($CDCl_3$) 0.99 [s, $(CH_3)_3C$], 2.38 ppm (CH_2).

Anal. Calcd for $C_{19}H_{33}BrO_3$: C, 58.60; H, 8.54; Br, 20.52. Found: C, 58.84; H, 8.41; Br, 20.21.

7-Chloro-1,3,5-tris(2-chloro-1,1-dimethylethyl)-2,4,9-trioxaadamantane.—Dropwise addition of stannic chloride (5 ml, 11.3 g, 0.043 mol) to 100 g (0.65 mol) of chloropivaloyl chloride[9] and 50 g (0.9 mol) of isobutylene at −15° produced an exothermic reaction and a viscous polymer layer separated. The mixture was allowed to stand for 16 hr. A few crystals in the liquid phase were filtered off. The polymer layer was extracted with hot acetone to yield a few more crystals. The yield of the trioxaadamantane was 0.5 g (0.5%): mp 156–157° from acetone; ir 2994, 2890 (CH), 1374, 1359 (*gem*-CH_3 groups), 1182, 1121, 1038 cm^{-1} (C–O–C–O–C); nmr ($CDCl_3$) 1.14 [s, $C(CH_3)_2$], 2.32 (s, ring CH_2), 3.67 ppm (s, CH_2Cl).

Anal. Calcd for $C_{19}H_{30}Cl_4O_3$: C, 51.01; H, 6.76; Cl, 31.71. Found: C, 51.07; H, 6.80; Cl, 31.57.

Passing isobutylene into a mixture of chloropivaloyl chloride and stannic chloride gave a similar result.

(7) Y. Yamase, *Bull. Chem. Soc. Jap.*, **34**, 480 (1961).
(8) Research Organic/Inorganic Chemical Corp., Sun Valley, Calif.
(9) F. Nerdel and U. Kretzschmar, *Justus Liebigs Ann. Chem.*, **688**, 61 (1965).

Registry No.—**4**, 35336-97-1; 2,2,5-trimethyl-4-hexen-3-one, 14705-30-7; 5-chloro-2,2,5-trimethyl-3-hexanone, 35336-99-3; 7-bromo-1,3,5-tri-*tert*-butyl-2,4,9-trioxaadamantane, 35337-00-9; 7-chloro-1,3,5-tris(2-chloro-1,1-dimethylethyl)-2,4,9-trioxaadamantane, 35337-01-0; isobutylene, 115-11-7.

Mononitration of Perylene. Preparation and Structure Proof of the 1 and 3 Isomers

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The limitations of the published method[1] for the preparation of 3-nitroperylene have recently been pointed out, and an improved procedure was disclosed employing attack by nitrite ion on the perylene radical cation.[2] These limitations have also led us to search for a better method of preparing this nitro compound. We wish to report a simple procedure that not only affords 3-nitroperylene in good yield, but also gives the previously unknown 1 isomer. Formation of the latter is of interest, since the only other example of substitution at position 1 occurred during the reaction of perylene with alkyllithium reagents.[3-5]

When perylene is nitrated in dioxane with dilute nitric acid, a mixture containing two mononitroperylenes is obtained. This mixture is readily separated by column chromatography into a rather insoluble, higher melting (210–212°) isomer (56%) and a lower melting (170–171°) isomer (24%). The higher melting isomer is identical with the compound obtained by the procedure of Dewar and Mole.[1] They proposed, but did not prove, that this compound was 3-nitroperylene (**1a**).

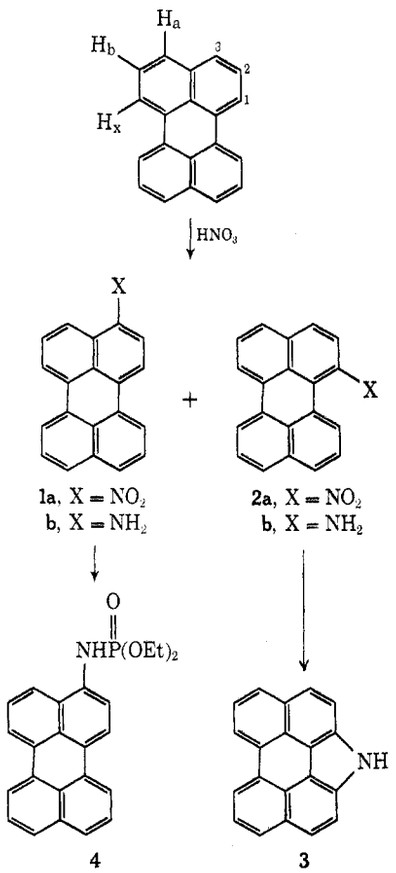
In order to make an unequivocal assignment of structure, the behavior of each isomer toward triethyl phosphite was examined. Only 1-nitroperylene should readily cyclize[6] to an amine. The 3 isomer should give tar,[6] or possibly a phosphoramidate, as observed with 4-dimethylaminonitrosobenzene.[7]

The lower melting isomer (170–171°) gave a good yield (82%) of amine **3** when heated with triethyl phosphite. The higher melting isomer gave a phosphorus-containing compound which is assigned structure **4**, based on its analysis ane spectral properties (Experimental Section). Thus the lower melting isomer is 1-

(1) M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956).
(2) C. V. Ristagno and H. J. Shine, *J. Amer. Chem. Soc.*, **93**, 1811 (1971).
(3) H. E. Zieger and J. E. Rosenkranz, *J. Org. Chem.*, **29**, 2469 (1964).
(4) H. E. Zieger and E. M. Laski, *Tetrahedron Lett.*, 3801 (1966).
(5) H. E. Zieger, *J. Org. Chem.*, **31**, 2977 (1966).
(6) J. I. G. Cadogan, *et al.*, *J. Chem. Soc.*, 4831 (1965).
(7) P. J. Bunyan and J. I. G. Cadogan, *ibid.*, 42 (1963).

TABLE I
NMR SPECTRA

Compd	Multiplicity	Area	Peak positions or range, τ	J, Hz	Assignment
Perylene (CS_2)	m	4	1.7–1.9		H_x
	m	8	2.3–2.8		$H_a + H_b$
3-Nitroperylene,	m	5	1.7–2.2		H_x
1a (DMSO-d_6)	m	6	2.4–2.8		$H_a + H_b$
3-Aminoperylene,	m	5	1.7–2.1		H_x
1b (DMSO-d_6)	m	5	2.4–2.8		$H_a + H_b$
	d	1	3.08 3.22	8.0	Proton adjacent to NH_2
	s	2	4.40		NH_2
1-Nitroperylene,	m	2	1.8–2.0		H_x
2a ($DCCl_3$)	m	9	2.3–2.8		$H_a + H_b$
1-Aminoperylene,	m	3	1.6–2.1		H_x
2b ($DCCl_3$)	m	7	2.4–2.8		$H_a + H_b$
	d	1	3.12 3.25	8.0	Proton adjacent to NH_2
	s	2	5.64		NH_2



nitroperylene (**2a**) and the higher melting isomer is 3-nitroperylene (**1a**), as originally suggested.[1]

The nmr spectra of the two mononitroperylenes and the corresponding amines (Table I) also support the proposed structures. The spectrum of perylene[8] is an ABX pattern, and consists of a low-field group of peaks (τ 1.7–1.9) for the four H_x atoms and a high-field group (τ 2.3–2.8) for the eight $H_a + H_b$ atoms. Both mononitroperylenes have these same two groups of peaks. The higher melting isomer (**1a**) has five protons in the H_x group instead of four, and six in the $H_a + H_b$ group instead of seven. This shift of one proton from the $H_a + H_b$ group to the H_x group is attributed to the peri interaction characteristic of 1-substituted naphthalenes;[9] proton 4 being deshielded by the presence of the 3-nitro substituent. The corresponding amine (**1b**) also has five protons in the H_x group, as expected.

The lower melting isomer (**2a**) has two protons in the H_x group instead of three and nine in the $H_a + H_b$ group instead of eight. Thus, one proton in the H_x group is shielded. This shift is attributed to the influence of the anisotropy of the nitro group on the proton at position 12. When the nitro group is reduced to the amino substituent (**2a** → **2b**), the shielding effect is removed and there are three protons in the H_x group.

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

Experimental Section[10]

Nitration of Perylene.—To a hot solution of 10 g (0.04 mol) of perylene in 120 ml of dioxane was added a mixture of 45 ml of water and 30 ml of nitric acid (d = 1.5). The resulting solution was heated on a steam bath for 1 hr, cooled, and poured into 2 l. of water. The solid was collected, washed, dried, dissolved in 130 ml of chlorobenzene, and chromatographed on 500 g of Florisil. Benzene eluted 0.1 g of perylene, followed by 2.8 g (24%) of brick-red 1-nitroperylene (**2a**). Methylene chloride eluted 6.6 g (56%) of similarly colored 3-nitroperylene (**1a**), mp 210–212°, which did not depress the melting point of a sample prepared by the method of Dewar and Mole.[1] 1-Nitroperylene was recrystallized from benzene (soluble)–ethanol: mp 170–171°; uv λ_{max} (ETOH) 255 nm (log ϵ 4.45), 393 (3.93), and 437 (4.08).

Anal. Calcd for $C_{20}H_{11}NO_2$: C, 80.8; H, 3.7; N, 4.7. Found: C, 80.7; H, 3.9; N, 4.7.

Treatment of 1-Nitroperylene with Triethyl Phosphite.—A mixture of 0.50 g (0.0017 mol) of 1-nitroperylene (**2a**) and 5 ml of triethyl phosphite was heated at reflux under nitrogen for 2 hr. Upon cooling to room temperature, the yellow-brown amine **3** crystallized: yield 0.36 g (82%); mp 360° dec; ir 3400 cm^{-1} (NH); nmr (DMSO-d_6) τ 5.35 (s, 1, NH) and 1.22–2.33 (m, 10, aromatic).

Anal. Calcd for $C_{20}H_{11}N$: C, 90.5; H, 4.2; N, 5.3. Found: C, 90.2; H, 4.4; N, 5.1.

Treatment of 3-Nitroperylene with Triethyl Phosphite.—A mixture of 1.0 g (0.0034 mol) of 3-nitroperylene (**1a**) and 10 ml of triethyl phosphite was heated at reflux under nitrogen for 1 hr, cooled, and chromatographed on Florisil. After removal of small amounts of material with benzene and methylene chloride, the phosphoramidate **4** was eluted with ethanol and recrystallized from chlorobenzene: yield 0.70 g (51%); mp 225° dec (depends upon rate of heating); nmr (DMSO-d_6) τ 1.7–2.0 (m, 5, aromatic)

(9) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(10) The nmr spectra were measured on a Varian Associates Model A-60 spectrometer and the uv spectrum on a Perkin-Elmer Model 202 spectrometer. All melting points are uncorrected.

2.4–2.8 (m, 7, aromatic and NH, one proton exchangeable with D_2O), 5.7–6.2 (pair of overlapping quartets, 4, methylene coupled to phosphorus), 8.77 (t, 6, methyl).

Anal. Calcd for $C_{24}H_{28}NO_3P$: C, 71.5; H, 5.5; N, 3.5; P, 7.7. Found: C, 71.6; H, 5.5; N, 3.5; P, 7.9.

1-Aminoperylene (2b).—Reduction of 1-nitroperylene (**2a**) was performed as described[1] for 3-nitroperylene, except that 1,2-dimethoxyethane proved to be a better solvent. A solution was prepared by heating 1.0 g (0.0034 mol) of 1-nitroperylene in 50 ml of 1,2-dimethoxyethane. About 100 mg of 10% palladium on charcoal was added, followed by 2 ml of 64% hydrazine. After the mixture had been heated for 3 min, the catalyst was removed and the solvent was distilled to leave a yellow solid. Recrystallization from a mixture of benzene (soluble) and ethanol gave 0.75 g (83%) of amine **2b**, mp 195–197°.

Anal. Calcd for $C_{20}H_{13}N$: C, 89.9; H, 4.9; N, 5.2. Found: C, 89.5; H, 4.5; N, 5.0.

The 3-amino compound[1] **1b** was prepared in better yield by using this solvent in place of ethanol.

Registry No.—**1a**, 20589-63-3; **1b**, 20492-13-1; **2a**, 35337-20-3; **2b**, 35337-21-4; **3**, 35337-22-5; **4**, 35337-23-6; perylene, 198-55-0.

Thallium in Organic Synthesis. XXXV. Oxidation of Cyclohexanones to Adipoins Using Thallium(III) Nitrate[1,2]

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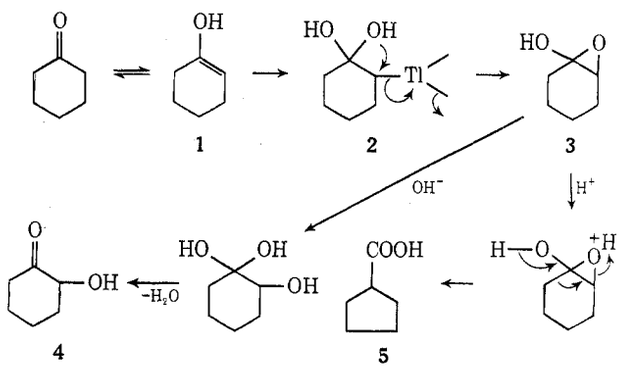
There are only four reports describing the reactions of cyclohexanones with thallium(III) salts. Oxidation with thallium(III) acetate in hot acetic acid has been found to result in α-acetoxylation in low yield,[3,4] but conflicting claims have been made as to the products formed using thallium(III) perchlorate in aqueous acidic media. Littler reported that cyclohexanone was converted first into adipoin and then into cyclohexane-1,2-dione.[5] In a later study, however, Wiberg and Koch found that the major product was cyclopentanecarboxylic acid (75%), and that only 3% of adipoin was obtained. They also showed that adipoin did not serve as the precursor for the ring-contracted product.[6] In view of this apparent duality in reaction pathway we have investigated the reaction of cyclohexanone with thallium(III) nitrate (TTN).[7]

Oxidation of cyclohexanone with TTN in acetic acid at room temperature proceeded rapidly, and precipitation of thallium(I) nitrate was complete in a few minutes. Filtration and neutralization of the filtrate with aqueous sodium bicarbonate solution followed by extraction with ether gave adipoin in 84% yield. This result at first sight confirmed Littler's claim; closer investigation of the reaction, however, revealed that the nature of the product formed on oxidation was temperature dependent. Thus, if oxidation was performed at room temperature, the thallium(I) nitrate was removed by filtration, and the filtrate was heated above about 40° for a few minutes, no adipoin was obtained. The sole product isolated, again in 84% yield, was cyclopentanecarboxylic acid.

That there were indeed two different reaction pathways was readily proved as follows. Oxidation of cyclohexanone was carried out as described above. The filtrate obtained after removal of the thallium(I) nitrate was divided into two equal portions. One of these was treated with aqueous sodium bicarbonate and gave adipoin (**4**). The other was heated for a few minutes and gave cyclopentanecarboxylic acid (**5**). Each product was uncontaminated by the other, thus indicating the intermediacy of a common precursor. Moreover, this precursor cannot be an organothallium derivative, as thallium(I) nitrate had been recovered in almost quantitative yield. It would therefore appear from the above results that both Littler and Wiberg and Koch may have been correct with respect to the products they isolated. There is little doubt, however, that the mechanism postulated by Wiberg for formation of the cyclopentanecarboxylic acid is incorrect, as it involved the intermediacy of an organothallium derivative.

We suggest that the mechanisms of these transformations are best represented as shown in Scheme I, and

SCHEME I



that the common precursor to **4** and to **5** is the epoxy enol **3**. Oxythallation of enols (*cf.* **1** → **2**) is a known process,[8] while Kruse and Bednarski have recently shown that epoxides may be prepared by oxidation of olefins with thallium(III) acetate.[9] Not unexpectedly, all attempts to isolate **3** from the reaction mixture were unsuccessful. One noteworthy feature of the mechanism shown in Scheme I is that water is involved as nucleophile in the oxythallation step; this must be the

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(5) J. S. Littler, *J. Chem. Soc.*, 827 (1962).

(6) K. B. Wiberg and W. Koch, *Tetrahedron Lett.*, 1779 (1966); we have confirmed this result.

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(9) W. Kruse and T. M. Bednarski, *J. Org. Chem.*, **36**, 1154 (1971).