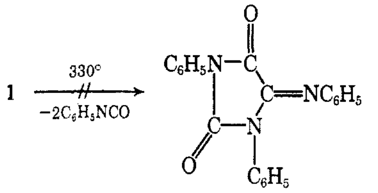
acid 5-anil (**5**). However, the pyrolysis product was shown not to be **5** by comparison with an authentic sample.



5

Experimental Section[10]

1,3,6,8,10-Pentaphenyl-1,3,6,8,10-pentazaspiro[4,5]decane-2,4,7,9-tetranone (1).—A solution of 3.7 g (0.05 mol) of N,N-dimethylformamide and 59.5 g (0.50 mol) of phenyl isocyanate was heated at 140–150° for 16 hr. Excess phenyl isocyanate was removed by distillation *in vacuo*. The residue was dissolved in boiling chloroform, the chloroform was removed by azeotropic distillation with ethanol, and the product was allowed to precipitate from ethanol. Thorough washing with ether gave colorless crystals, containing alcohol of crystallization, which after drying at 100° (3 mm) for 24 hr consisted of 28.5 g (96%) of **1**: mp 228–230° (unchanged by recrystallization); ir (KBr), 1790 (C═O), 1730 (C═O), 1685 cm^{-1} (C═O); nmr (CDCl$_3$), δ 7.0–8.1 (m, 23) 6.5–6.7 (m, 2). This unusual distribution of nmr signals was also observed by Ulrich, *et al.*[2]

Anal. Calcd for $C_{35}H_{25}N_5O_4$: C, 72.53; H, 4.32; N, 12.09; O, 11.05; mol wt, 579. Found: 72.84; H, 4.27; N, 12.26; O, 10.91; mol wt (mass spectroscopy), 579.

The same compound resulted in lower yield when prepared at 75–85°. Cyclohexyl isocyanate and phenyl isothiocyanate failed to react at 140–150°.

1,3,6,8,10-Penta-*p*-methoxyphenyl-1,3,6,8,10-pentazaspiro[4,5]decane-2,4,7,9-tetraone (2).—This derivative was prepared in the same way as **1**, from the reaction of 0.05 mol of N,N-dimethylformamide with 0.50 mol of *p*-methoxyphenyl isocyanate. The yield of **2** was 34.0 g (93%), mp 286–287°, when dried. Recrystallization from ethanol–acetonitrile (2:1) raised the melting point to 287–288°.

Anal. Calcd for $C_{40}H_{35}N_5O_9$: C, 65.83; H, 4.83; N, 9.59. Found: C, 65.79; H, 4.78; N, 9.48.

2-Dimethylamino-1,3,5-triphenylhexahydro-1,3,5-triazine-4,6-dione (3).—A solution of 24.0 g (0.16 mol) of N-phenyl-N′,N′-dimethylformamidine[4] and 34.0 ml (0.32 mol) of phenyl isocyanate was heated at 80–85° for 12 hr. The resulting solid, after washing with ether, consisted of 40.0 g (64%) of **3**, mp 178–179°. Recrystallization from methanol and drying at 60° *in vacuo* (3 mm) for 12 hr raised the melting point to 181–182°: ir (KBr), 1712 (C═O), 1663 cm^{-1} (C═O); nmr (CDCl$_3$), δ 2.4 (s, 6, (CH$_3$)$_2$N), 5.95 (s, 1, C—H), 7.0–7.7 (m, 15, C$_6$H$_5$).

Anal. Calcd for $C_{23}H_{22}N_4O_2$: C, 71.50; H, 5.74; N, 14.50. Found: C, 71.84; H, 5.95; N, 14.62.

2-[1-(1-Phenyl-3,3-dimethylureido)]-1,3,5-triphenylhexahydro-1,3,5-triazine-4,6-dione (4).—A mixture of 3.0 g (0.0078 mol) of **3** and 15 ml (0.138 mol) of phenyl isocyanate was heated at 80–95° for 18 hr. The solid crystalline product, after washing with ether, consisted of 1.8 g (46%) of **4**, mp 239–240°. Recrystallization from ethanol and drying *in vacuo* at 60° for 24 hr gave tiny white needles melting at 242–243°: ir (KBr), 1712 (C═O), 1662 (C═O), 1655 cm^{-1} (C═O); nmr (CDCl$_3$), δ 2.4 (s, 6, (CH$_3$)$_2$N), 6.32–6.70 (m, 2, C$_6$H$_5$), 7.0–8.0 (m, 19, C$_6$H$_5$ and CH); mass spectrum (70 eV) *m/e* 342, 194, 164, 119, 91, 72.

Anal. Calcd for $C_{30}H_{27}N_5O_3$: C, 71.01; H, 5.32; N, 13.81. Found: C, 71.07; H, 5.41; N, 14.01.

Acid hydrolysis of **4** gave N,N′,N″-triphenylbiuret (95%), mp 150–151°.

Compound **4** was converted into **1** by heating a mixture of 2.0 g (0.004 mol) of **4** with 15 ml (0.138 mol) of phenyl isocyanate at 140–150° for 3 hr. The excess phenyl isocyanate was removed under reduced pressure, the residual gum was stirred with acetone, and the resulting precipitate was ground with ether and dried as before. The yield was 2.1 g (91%) of product, mp 228–230°, undepressed by mixing with **1**.

The acetone filtrate on evaporation yielded a gummy residue which was extracted three times with boiling water. The cooled aqueous extracts yielded needles (0.5 g, 76%) of 1-phenyl-3,3-dimethylurea, mp 129–130° (undepressed on mixture melting with an authentic sample).

Pyrolysis of 1.—Heating of 21.2 g (0.036 mol) of **1** at 330–360° and at a pressure of 50 mm gave as distillate 8.4 g (0.071 mol) of phenyl isocyanate. The residue, washed with acetone and recrystallized from methylene chloride, gave 11.0 g of a white solid **5**, which did not melt below 360° and was not hydrolyzed by aqueous alcoholic HCl: ir (KBr), 1705 (C═O), 1740 cm^{-1} (C═O).

Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.88; H, 4.42; N, 12.30; mol wt, 341. Found: C, 73.61; H, 4.40; N, 12.34; mol wt, 357 (boiling point elevation in bromobenzene).[11]

1,3-Diphenylparabanic Acid 5-Anil (5).—A mixture of 17.0 g (0.050 mol) of 1,3-diphenyl-5,5-diethoxyhydantoin,[12] 5.0 g (0.053 mol) of aniline, and 1 drop of concentrated HCl was heated at 135–140° for 1.5 hr with continuous distillation of the ethanol as formed. The resulting yellow glass was dissolved in a large volume of ether and treated with dry HCl to precipitate the hydrochloride. Decomposition of the hydrochloride with water gave 15.0 g (89%) of the free anil, a yellow solid melting at 105–108°. The compound was recrystallized from petroleum ether (bp 30–60°)–ethanol (2:1) with difficulty; after drying *in vacuo* at 50° for 12 hr, it melted at 122–123°: ir (KBr), 1792 (C═O), 1742 (C═O), 1672 cm^{-1} (C═N).

Compound **5** was hydrolyzed in aqueous ethanolic HCl to aniline hydrochloride and 1,3-diphenylparabanic acid.

Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.88; H, 4.42; N, 12.30. Found: C, 74.22; H, 4.76; N, 12.01.

Registry No.—**1**, 17350-46-8; **2**, 17350-47-9; **3**, 17350-48-0; **4**, 17350-49-1; **5**, 17350-50-4.

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[10] Melting points (corrected) determined on a Fisher-Johns apparatus; ir spectra on Perkin-Elmer 337 or 137 spectrophotometer; nmr spectra on a Varian A-60A spectrometer with TMS as internal standard, mass spectra on a 21-110B CEC double focus mass spectrometer.

[11] Subsequent mass spectral data suggest that the pyrolysis product has a molecular weight twice that found by boiling point elevation.

[12] C. W. Whitehead and J. Traverso, *J. Amer. Chem. Soc.*, **80**, 962 (1958).

The Reaction of Ethylene- and Propylenediamine with Esters of Trihaloacetic Acids

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The dihydroimidazole **1** was reportedly prepared by the reaction of ethyl trichloroacetate with ethylenediamine.[1] Several attempts to repeat this preparation gave a product whose melting point was similar to that reported for **1**, but which was, in fact, compound **2** (X = Cl) as shown by its ir and nmr spectra, elemental analyses, and molecular weight. Compound **2** (X = Cl) was the only product isolated (80% yield) under a variety of reaction conditions. The product from the reaction of trichloroacetyl chloride and ethylenediamine was identical with that from the above reaction, *i.e.*, **2** (X = Cl).

The ir spectrum of 1,6-bis(trichloroacetamido)hexane, prepared by the reaction of hexamethylenediamine with ethyl trichloroacetate,[2] was completely analogous to that of **2** (X = Cl). Cyclization would not compete with bisamide formation in this case.

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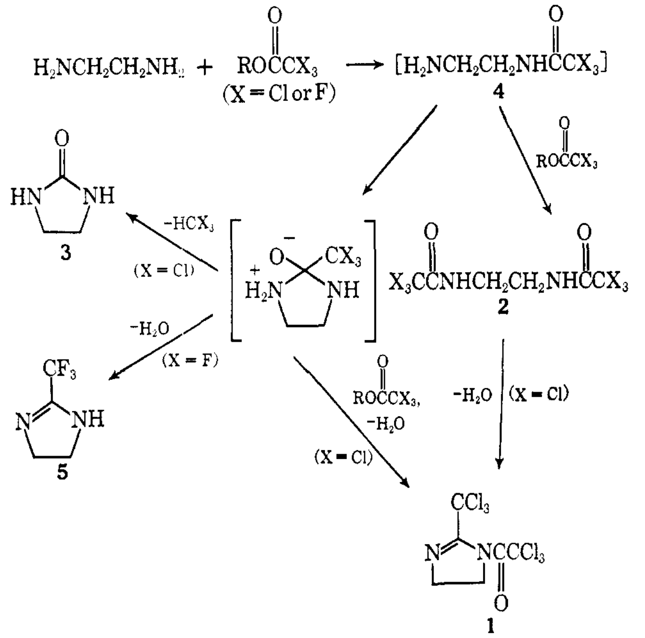
[1] M. M. Joullie and A. R. Day, *J. Amer. Chem. Soc.*, **76**, 2990 (1954).

[2] A. R. Surrey and J. R. Meyer, *J. Med. Pharm. Chem.*, **3**, 419 (1961).

Likewise, the ir spectrum of 1,2-bis(trifluoroacetamido)-ethane, 2 (X = F), obtained from methyl trifluoroacetate and ethylenediamine,[1] was also analogous to that of 2 (X = Cl).

In one attempt to prepare **1**, methyl trichloroacetate was added to excess ethylenediamine at ambient temperature with subsequent refluxing and distillation. The only isolable products were 2-imidazolidone (**3**) and chloroform, similar to results reported by Baganz and Domaschke.[3]

Boiling 2 (X = Cl) in concentrated hydrochloric acid for 7 hr resulted in the hydrolysis of about 44% of the bisamide, the remainder being isolated unchanged.



Although compound **1** was not isolated from the reaction of ethylenediamine and ethyl trichloroacetate in the present work, even under conditions which approximate as closely as possible those which are reported to give it, its structure is strongly supported by elemental analyses.[1] It is concluded, therefore, that under many conditions 2 (X = Cl) rather than **1** is likely to be the product of this reaction.

This observation leads to a reinterpretation of the reaction of ethylenediamine and ethyl trichloro- and trifluoroacetates.[3] The initial intermediate is **4**,[4] which, depending on conditions, may react with additional ester to give the bisamide **2** or may react intramolecularly to give a cyclic intermediate which subsequently yields **5** or **3** depending on the nature of X, *i.e.*, **5** is obtained when X is F,[3] and **3** when X is Cl. These results are not surprising in view of previous work which provides a basis for comparing the relative efficacies of the trifluoromethyl and trichloromethyl anions as leaving groups.[1,3,5,6] Under certain conditions either **2** or the cyclic intermediate may react to give **1**.[1]

Propylenediamine with ethyl trichloroacetate gives the bisamide homologous to 2 (X = Cl) rather than the reported methyl homolog of **1**.[1] The reaction of this diamine with esters of tribromo-, trifluoro-, dichlorofluoro- and chlorodifluoroacetic acid has been found to give, in each case, the corresponding bisamide as the only isolable product. In the case of tribromo compound, bromoform was also detected, indicating the occurrence of reactions in addition to amide formation.

Experimental Section

The ir spectra were obtained on a Perkin-Elmer 21 Infrared spectrophotometer. The nmr spectra were obtained on a Varian A-60 instrument. The glpc analyses were carried out using an Aerograph A-90-P instrument with a 5 ft 10% Dow 710/acid washed C/W at 127° and a helium pressure of 27 psig. The melting points are uncorrected. The molecular weight was determined ebullioscopically. The ethylene- and propylenediamines were products of the Union Carbide Corp. and contained a maximum of 0.1% of water. The ethanol (Union Carbide Corp. "200 proof") contained a maximum of 50 ppm of water. The diamines and the ethanol were passed through, and stored over, 13X molecular sieves prior to use. The ethyl and methyl trichloroacetates were Eastman White Label materials used with or without distillation without detectable difference. The ethyl tribromoacetate,[7] bp 107–114° (20 mm), was prepared by the acid-catalyzed reaction of ethanol and tribromoacetic acid. Methyl dichlorofluoro- and chlorodifluoroacetates were supplied by Dr. L. O. Moore and ethyl trifluoroacetate was either Eastman White Label or supplied by Dr. J. P. Henry of these laboratories.

1,2-Bis(trichloroacetamido)ethane (2, X = Cl). A. From Ethylenediamine and Methyl Trichloroacetate.—To a solution of 142 g (0.8 mol) of methyl trichloroacetate in 150 ml of ethanol was slowly added with stirring a solution of 24 g (0.4 mol) of ethylenediamine in 150 ml of ethanol. A white solid began to separate almost immediately. When addition was complete, the suspension was stirred overnight at room temperature, and the solid then collected and air dried to give 114 g (81%) of white crystals, mp 209–211°. Recrystallization from methyl Cellosolve gave a material: mp 208–210° (lit.[1] for **1**, mp 206–207°); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.03, 6.05 (NH), 5.93 (C=O), 12.15, 12.52 μ (CCl_3). The nmr spectrum was difficult to obtain because of insolubility, but a weak spectrum was finally obtained (*d*-acetone) which exhibited a partially resolved A_2B_2 pattern at δ 3.62 (*J* ~2 cps) assigned to $>NCH_2CH_2N<$ and a broad poorly defined singlet at 9.1 (NH). Addition of hydrogen chloride vapors coalesced the A_2B_2 pattern to a singlet at 3.62.

Anal. Calcd for $C_6H_6Cl_6N_2O_2$: C, 20.54; H, 1.72; N, 7.99; Cl, 60.63; mol wt, 351. Found: C, 20.42; H, 1.52; N, 7.75; Cl, 60.80; mol wt, 343 ± 3%.

B. From Trichloroacetyl Chloride.—To a solution of 12 g (0.2 mol) of ethylenediamine in 50 ml of absolute ethanol was added dropwise, with stirring, 18.2 g (0.1 mol) of trichloroacetyl chloride during which time a solid separated. The mixture was stirred overnight and then chilled. The solid was collected, thoroughly washed with water, and air dried to give 7.5 g (43%) of 2 (X = Cl), mp 209–211°. The ir spectrum was identical with that of the product from **A**.

1,6-Bis(trichloroacetamido)hexane.—Using procedure A, 8.3 g (0.05 mol) of hexamethylenediamine and 18.1 g (0.1 mol) of ethyl trichloroacetate in 20 ml of ethanol gave 13 g (64%) of product, mp 155–156° (lit.[2] mp 155–156°). The ir spectrum was analogous to that of 2 (X = Cl).

Reaction of Methyl Trichloroacetate with Excess Ethylenediamine. 2-Imidazolidone 3.—To 300 g (5 mol) of ethylenediamine (containing about 1% water) was added dropwise with stirring over 1 hr 89 g (0.5 mol) of methyl trichloroacetate. After stirring at room temperature for 24 hr, the mixture was slowly distilled to give 14 g of distillate, bp 29–38° (110–140 mm), which was shown by glpc analyses to be 90% chloroform, 6% water, and 4% ethylenediamine. The distillation was continued to a kettle temperature of 150° at 6 mm. The residue, 48 g, was flash distilled to give 39 g of dark material, bp 135–165° (0.5–1 mm), mp 98–115°. Recrystallization from

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[3] H. Baganz and L. Domaschke, *Angew. Chem. Intern. Ed. Engl.*, **2**, 692 (1963).

[4] Ch. Cloëz [*Ann. Chem. Phys.*, [6] **9**, 218 (1886), in F. K. Beilstein's, "Handbuch der organischen Chemie," Vol. 4, 1st ed, 1922, p 250] reports the reaction of ethylenediamine and hexachloroacetone to give **4** (X = Cl). The melting point reported by this material (200°, from ethanol) indicates that the product was most probably **2** (X = Cl).

[5] A. C. Pierce and M. M. Joullie, *J. Org. Chem.*, **28**, 658 (1963).

[6] L. H. Slough and E. Bergmann, *ibid.*, **26**, 3158 (1961).

[7] C. Broche, *J. Prakt. Chem.*, (2) **158**, 97 (1894).

ethanol gave 18.5 g (43%) of **3**, mp 130–132.5° (lit.[8] mp 131°). The ir spectrum was identical with a reference scan.

Hydrolysis of 2 (X = Cl).—A mixture of 9 g (0.025 mol) of **2** (X = Cl) was suspended in 100 ml of concentrated hydrochloric acid and was heated at reflux with stirring for 7 hr. Complete solution did not occur. After cooling at room temperature overnight the solid was collected, washed thoroughly with water, and air dried to give a 5-g (56%) recovery of the starting material, mp 210.5–212.5°, whose ir spectrum was unchanged.

The filtrate was evaporated *in vacuo* at 50–60° to give 1.5 g of residue, which, upon recrystallization from 4:1 ethanol–water gave 0.8 g of ethylenediamine dihydrochloride, mp 325–327° dec (lit.[1] mp 327° dec). Based on a 4-g loss of **2** (X = Cl) this represents a 62% recovery of dihydrochloride.

1,2-Bis(trichloroacetamido)propane.—Using procedure A, 88 g (1.2 mol) of propylenediamine in 450 ml of ethanol was allowed to react with 426 g (2.4 mol) of methyl trichloroacetate in 450 ml of ethanol to give 361 g (82%) of product: mp 201–202° (lit.[1] mp 196–197°); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.02, 6.53 (NH), 5.91 (C=O), 12.15 μ (CCl_3).

Anal. Calcd for $C_7H_8Cl_6N_2O_2$: C, 23.04; H, 2.21. Found: C, 22.89; H, 2.34.

Using procedure A the following amides were prepared.

1,2-Bis(tribromoacetamido)propane.—Propylenediamine (0.02 mol) and 0.04 mol of ethyl tribromoacetate in 16 ml of ethanol gave 1.5 g (11.9%) of product: mp 201.5–203° (isopropyl alcohol); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 2.99, 6.65 (NH), 5.95 (CO), 16.6 μ (CBr_3).

Anal. Calcd for $C_7H_8Br_6N_2O_2$: C, 13.31; H, 1.26; N, 4.44. Found: C, 13.90; H, 1.18; H, 4.61.

Bromoform was shown to be present in the ethanol filtrate from the crude amide by glpc analysis.

1,2-Bis(trifluoroacetamido)propane.—Propylenediamine (0.05 mol) and ethyl trifluoroacetate (0.1 mol) in 18 ml of ethanol gave 5 g (38%) of product: mp 146–148°; $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.0, 6.38 (NH), 5.79, 5.87 (CO), 8.26, 8.37, 8.67 μ (CF_3).

Anal. Calcd for $C_7H_8F_6N_2O_2$: N, 10.53. Found: N, 10.98.

1,2-Bis(chlorodifluoroacetamido)propane.—Propylenediamine (0.05 mol) and methyl chlorodifluoroacetate (0.1 mol) gave 3 g (20%) of product: mp 132–136° (isopropyl ether–hexane); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.06 6.43 (NH), 5.93 (CO), 8.5, 8.8 (CF), 13.6, 14.5 μ (CCl).

Anal. Calcd for $C_7H_8Cl_2F_4N_2O_2$: N, 9.37; Found: N, 9.27.

1,2-Bis(dichlorofluoroacetamido)propane.—Propylenediamine (0.045 mol) and 0.09 mol of methyl dichlorofluoroacetate in 20 ml of ethanol gave 4.5 g (26%) of product: mp 171–173° (ethanol); $\lambda_{\max}^{1\%\ \mathrm{KBr}}$ 3.02, 6.45 (NH), 5.87 (CO), 9.23 (CF), 11.6, 15.15 μ (CCl).

Anal. Calcd for $C_7H_8Cl_4F_2N_2O_2$: N, 8.44. Found: N, 8.66.

Registry No.—Ethylenediamine, 107-15-3; propylenediamine, 78-90-0; **2** (X = Cl), 17408-50-3; **3**, 120-93-4; 1,2-bis(trichloroacetamido)propane, 17408-51-4; 1,2-bis(tribromoacetamido)propane, 17408-52-5; 1,2-bis(trifluoroacetamido)propane, 17408-53-6; 1,2-bis(chlorodifluoroacetamido)propane, 17408-54-7; 1,2-bis(dichlorofluoroacetamido)propane, 17408-55-8.

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[8] E. Fischer and A. Koch, *Ann.*, **232**, 277 (1886).

A New Synthesis of Triptycene Systems[1]

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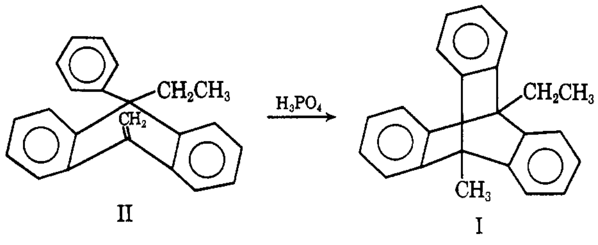
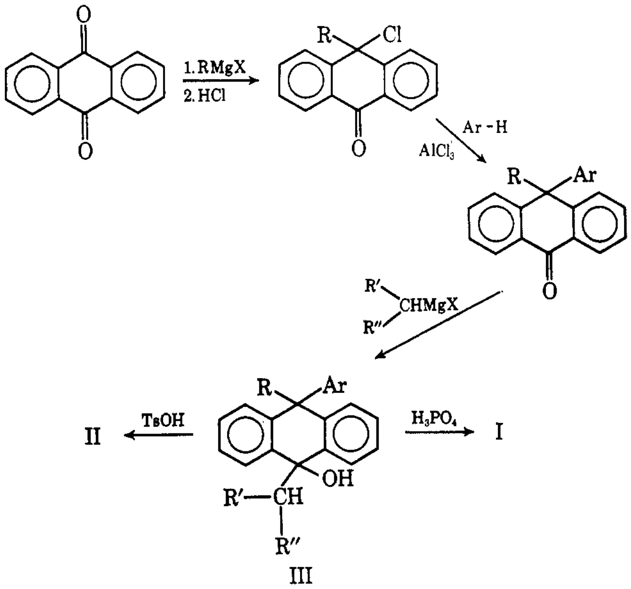
Syntheses of triptycene and substituted triptycenes have been limited to the use of Diels–Alder-type condensations using benzyne intermediates or quinones as the dienophile and anthracenes as the diene. There have also been some limited studies to prepare substituted triptycenes by carrying out electrophilic substitutions on triptycene itself.[2] A serendipitous observation in our laboratory has led to a synthesis of triptycene which has the potential for the preparation of a wide variety of triptycene derivatives. The discovery that 9-ethyl-10-methyltriptycene (I) is formed in excellent yield when 9-phenyl-9-ethyl-10-methylene-9,10-dihydroanthracene (II) is placed in polyphosphoric acid is the basis of this new synthesis. This reaction is not surprising in view of the required boat conformation of the 9,10-dihydroanthacene system and the resulting close proximity of the diaxial positions of C-9 and C-10.



The synthesis of the starting material (II) is straightforward and proceeds in good yield starting from anthraquinone. Moreover, it is not necessary to use II since its precursor (*i.e.*, III, R′ = R″ = H) gives identical results.



The variability of substitution patterns and the different types of substituents that can be employed is readily apparent. Furthermore, in the Friedel–Crafts step one could use substituted aromatics or even polynuclear aromatics which would lead to even more diverse substitution patterns as well as to entirely different types of systems.

No further experimental work to utilize this type of triptycene synthesis is planned. However, many different aspects of the chemistry of II are under active investigation.

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[1] This work was supported by Public Service Research Grant No. CA 04065-10 from the National Cancer Institute.

[2] C. Paget and A. Burgar, *J. Org. Chem.*, **30**, 1329 (1965), and references cited therein.