1645, 1580, 1475, 1440, 1435, 1420, 1390, 1350, 1265, 1100, 1070, 1045, 1030, 950, and 860 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 1.6–2.7 (m, 10 H), and 7.1–7.6 (m, 10 H); MS, *m/e* (relative intensity) 353 (1.3), 352 (5.9, M^+), 243 (89.7), 215 (100), 109 (38.8), 105 (35.3), 91 (31.3), 79 (31.4), and 77 (31.9). Anal. Calcd for $C_{21}H_{20}OS_2$: C, 71.55, H, 5.72, S, 18.19. Found: C, 71.54; H, 5.77; S, 18.08], and elution with 30% ether–hexane gave 700 mg (16%) of crude 3-(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (**14**), which, after purification by preparative TLC, showed identical spectral properties with those reported above.

Preparation of 3-Methyl-3-(phenylsulfenyl)bicyclo-[4.3.0]-1(6)-nonen-2-one (15). Sodium hydride (0.04 g, 1.0 mmol) in a 60% oil dispersion was washed with hexane under nitrogen to remove the oil. Dry THF (20 mL) was added, and the slurry was cooled to 0 °C. A solution of 0.25 g (1.02 mmol) of enone **14** in 5 mL of THF was added dropwise with stirring over 5 min. The mixture was stirred at 0 °C for 45 min, and then 2.7 g (3.2 mmol) of methyl iodide was added. The mixture was stirred for 5 min and treated with 5 mL water. The layers were separated and the water layer was washed with three 20-mL portions of ether. The combined ethereal extracts were washed with 20 mL of water and 20 mL of brine and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give 0.21 g (81%) of 3-methyl-3-(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (**15**) as an oil. The oil was purified by preparative TLC on silica gel plates using 50% ether–hexane as the eluting solvent to give **15** as a pale yellow oil with identical spectral properties with those reported above.

Supplementary Material Available: Information on data collection and structure solutions, tables of positional parameters, anisotropic temperature factors, bond angles, and interatomic distances for compounds **2**, **9**, and **14** (18 pages). Ordering information is given on any current masthead page.

Syntheses of Cyclopentene-Fused Polynuclear Aromatic Hydrocarbons

Ying-Sheng Chung, Henry Kruk, Ophelia M. Barizo, Morris Katz, and Edward Lee-Ruff*

Department of Chemistry, York University, Toronto, Ontario, Canada M3J 1P3

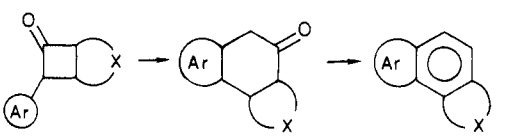
Received July 30, 1986

Regioselective α or β ring opening of bicyclic α-arylcyclobutanones permits the synthesis of linear and angular cyclopentene-fused polynuclear aromatic hydrocarbons (PAH), respectively. The syntheses of the cyclopentene-fused PAHs, aceanthrylene, acephenanthrylene, benz[*a*]aceanthrylene, and benz[*e*]acephenanthrylene are detailed utilizing this novel methodology.

Current interest in the environmental presence and toxicological properties of cyclopenta[*cd*]pyrene has stimulated work on the synthesis and chemical and biological properties of related cyclopentene-fused polynuclear aromatic hydrocarbons (PAHs).[1-3] Recently aceanthrylene (**1**) and acephenanthrylene (**4**), two non-bay-region PAHs, have been found to exhibit mutagenic activity[4,5] and along with the interest in their excited-state properties,[6] at least five reports of their synthesis have appeared.[4,7-10] Several years ago we developed a method for the preparation of PAHs incorporating cyclopentenes and heterocyclic rings via α-arylcyclobutanones substituted at the β-position with charge-stabilizing groups.[11,12] The method is based on the selective acid-catalyzed β ring opening (Scheme I) and lead to angular fused PAH derivatives. α-Arylcyclobutanones **2** are readily obtained from the cycloaddition of aryl ketenes with the appropriate olefin.

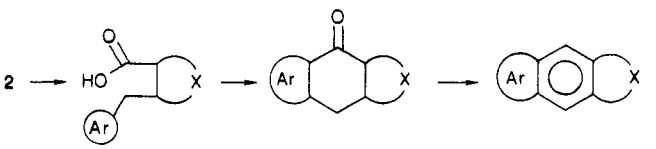
In addition to acid-catalyzed β ring opening, selective α ring opening reactions of cyclobutanones are known to occur under basic conditions[13] and reaction of **2** under these conditions would provide α-arylbutanoic acids **3**. Cyclization of **3** would result in α-tetralones which could be readily converted to linear fused PAHs (Scheme II). Therefore, the use of the bicyclic α-arylcyclobutanones, **2**, in such schemes would provide divergent syntheses of angular and linear fused polycyclics from common intermediates. In this study we report the syntheses of aceanthrylene (**1**), acephenanthrylene (**4**), and the benzoannelated derivatives benz[*a*]aceanthrylene (**5**) and benz[*e*]acephenanthrylene (**6**) using the above methodology.

Scheme I



2

Scheme II



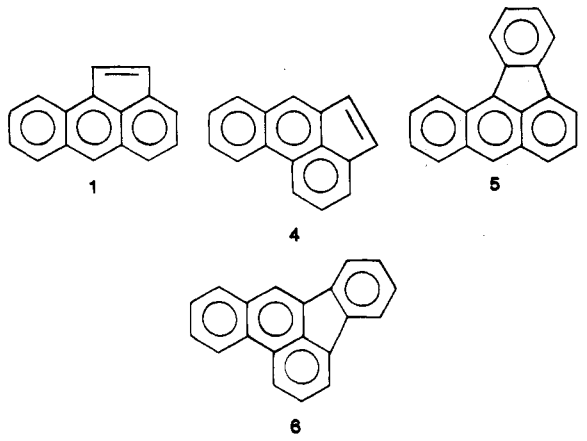
3

Results and Discussion

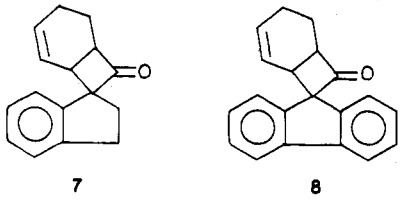
The key intermediates in these syntheses are the cyclobutanones **7** and **8**, which are readily prepared from cycloaddition of the corresponding ketenes with a 4- to 5-fold excess of 1,3-cyclohexadiene in benzene solution.

(1) Sangaiah, R.; Gold, A.; Toney, G. E. *J. Org. Chem.* **1982**, *48*, 1632.
(2) Sangaiah, R.; Gold, A.; Toney, G. E.; Toney, S. H.; Claxton, L.; Easterling, R.; Nesnow, S. *Mutat. Res.* **1983**, *119*, 259.
(3) Lee-Ruff, E.; Kruk, H.; Katz, M. *J. Org. Chem.* **1984**, *49*, 553.
(4) Amin, S.; Balanikas, G.; Huie, K.; Hussain, N.; Geddie, J. E.; Hecht, S. S. *J. Org. Chem.* **1985**, *50*, 4642.
(5) Nesnow, S.; Gold, A.; Mohapatra, N.; Bryant, B. J.; Rudo, K.; MacNair, P.; Ellis, S.; Gupta, R. Symposium on Polynuclear Aromatic Hydrocarbons Abstracts, 1985, Columbus.
(6) Plummer, B. F.; Hopkinson, M. J. H.; Zoeller, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 6779.
(7) Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1985**, *50*, 277.
(8) Scott, L. T.; Reinhardt, G.; Roelofs, N. H. *J. Org. Chem.* **1985**, *50*, 5886.
(9) Sangaiah, R.; Gold, A. *Org. Prep. Proced. Int.* **1985**, *17*, 53.
(10) Plummer, B. F.; Al-Saigh, Z. Y.; Arfan, M. J. *J. Org. Chem.* **1984**, *49*, 2069.
(11) Lee-Ruff, E.; Hopkinson, A. C.; Dao, L. H. *Can. J. Chem.* **1981**, *59*, 1675.
(12) Duperrouzel, P.; Lee-Ruff, E. *Can. J. Chem.* **1980**, *58*, 51.
(13) Trost, B. M.; Bogdanowicz, M. J.; Kern, J. *J. Am. Chem. Soc.* **1975**, *97*, 2218.

0022-3263/87/1952-1284$01.50/0

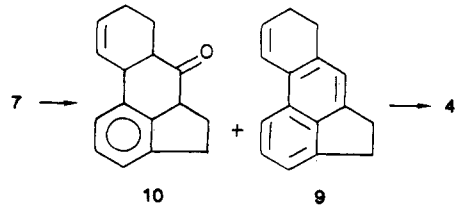


The ketenes were generated in situ by dehydrochlorination of the corresponding carboxylic acid chlorides with triethylamine. Best yields of the cycloadducts were obtained when the cycloaddition reaction was carried out under reflux in which case the ketene dimerization products were minimized. Only a single regioisomer was obtained in each case. The structures **7** and **8** were assigned on the basis

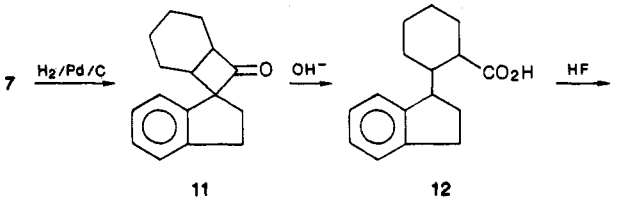


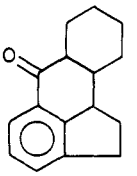
of analogy with previous studies on ketene cycloadditions to 1,3-dienes in which bond formation of the carbonyl carbon with the more nucleophilic terminal vinyl carbon is usually observed.[14]

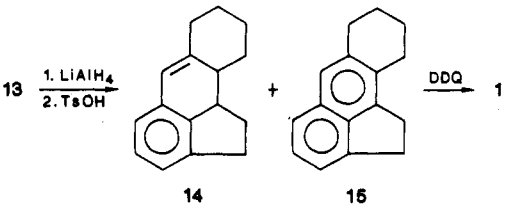
Addition of an ether solution of **7** to neat methanesulfonic acid generates a nonpolar material to which we assign the structure **9** on the basis of the parent ion observed in the mass spectrum and the similarity of the UV/visible spectrum with that of naphthalene. The expected ketone **10** was also present in the reaction mixture as a minor component. The formation of **9** could arise from ketone **10** by a 1,3-hydride shift and dehydration mechanism postulated for a similar transformation observed previously.[12] Dehydrogenation of **9** with 3 equiv of DDQ furnished **4** in 40% yield. The overall isolated yield based on starting 1-indanecarboxylic acid was 15%. The UV/visible, NMR spectra and melting point of **4** were identical with those reported for acephenanthrylene.[15] Acephenanthrylene (**4**) could also be obtained from ketone **10** by reduction with $LiAlH_4$ and dehydration/dehydrogenation with DDQ; the yields for conversion of **10** to **4** were slightly lower, resulting in an overall yield of about 10%.



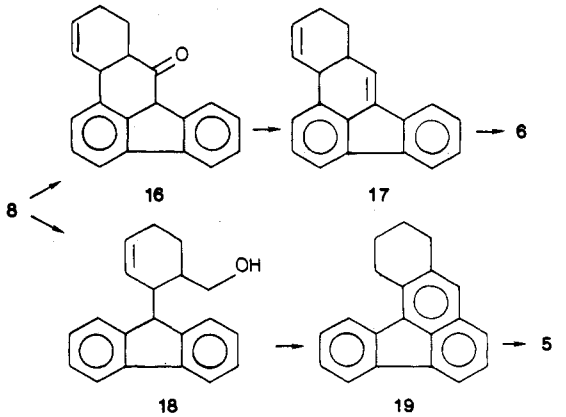
Hydrogenation of **7** followed by treatment of the dihydro derivative **11** with potassium hydroxide led to the carboxylic acid **12** (94% yield). Cyclization of this acid to **13** was accomplished by treatment with liquid HF. α-Tetralone **13** was reduced with $LiAlH_4$, and the resulting alcohol was dehydrated with toluenesulfonic acid or sulfuric acid to yield the octahydro derivative **14**. The hexahydro derivative **15** was obtained as a byproduct upon prolonged reaction times. The octahydro derivative **14** could be obtained in higher yield when the dehydration was carried out in sulfuric acid at room temperature for 5 min (85% yield). Dehydrogenation of **14** to aceanthrylene (**1**) was affected by using 4 equiv of DDQ. The product was identical with an authentic sample of aceanthrylene (**1**).[16]







The preparation of the benzo derivatives **5** and **6** proceeded along similar routes. The fluorenylketene–1,3-cyclohexadiene adduct **8** underwent rearrangement to the pentacyclic ketone **16** in methanesulfonic acid. The product mixture yielded a small amount of fluorenone. Hydride reduction of **16** and subsequent dehydration of the resultant alcohol gave the tetrahydro benz[*e*]acephenanthrylene **17**. Aromatization to **6** was accomplished by using excess DDQ. The overall yield based on starting ketone for this conversion was 14%. The product was identical in all respects with an authentic sample.[17] The linear benz[*a*]aceanthrylene was prepared by starting with ketone **8** and subjecting it to α-ring opening with $NaBH_4$ to give alcohol **18** along with a small amount of fluorenone.



(14) Burke, L. A. *J. Org. Chem.* **1985**, *50*, 3149.
(15) Laarhoven, W. H.; Cuppen, T. J. H. M. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 165.
(16) We thank Professor B. F. Plummer for providing us with a sample of **1** for comparison.
(17) Sample obtained from Chem. Service, West Chester, PA 19380.

It is interesting to note that, in contrast to ketone **8**, hydride reduction of cyclobutanone **7** with either sodium borohydride or lithium aluminum hydride proceeded to give a cyclobutanol.[18] The enhanced stability of the aromatic 9-fluorenyl anion intermediate formed upon α-cleavage of ketone **8** and relief of steric strain are most likely the driving forces for this type of reaction. The formation of fluorenone can be rationalized in terms of decomposition of a hydroperoxide formed from oxygenation of this anion. Cyclization of alcohol **18** to the tetrahydrobenz[*a*]aceanthrylene **19** could be carried out by using liquid hydrogen fluoride. It is interesting that dehydrogenation accompanies this dehydration reaction. Dehydrogenation of **19** was readily accomplished with excess DDQ; the overall yield of **5** from **8** was 28%.

Summary

The method of using α-aryl bicyclic cyclobutanones as intermediates constitutes a novel approach to the synthesis of polynuclear aromatic hydrocarbons incorporating cyclopentenes. Regioselective α or β ring opening of these derivatives permits the preparation of both linear and angular fused polycyclic systems. We have also previously shown that PAHs containing oxygen heterocyclic rings such as furans and pyrans can be readily obtained by using this methodology.[12] With the availability of benzo fluorenes[19] and their 9-carboxylic acid derivatives, it will be possible to prepare compounds such as **5** possessing "fjiord" regions for toxicological and analytical studies.

Experimental Section

Melting points (mp) were determined on a Reichert melting point apparatus and were uncorrected. Infrared (IR) spectra were recorded on a Unicam SP-1000 instrument as thin films or KBr pellets. Ultraviolet (UV) spectra were measured on a Unicam SP800-A spectrometer and Hewlett Packard 8451A diode array spectrophotometer. Proton NMR spectra were recorded on a Varian EM360 (60 MHz), CFT-20 (80 MHz), and Bruker AM-300 (300 MHz) spectrometers using samples dissolved in $CDCl_3$ containing 1% Me_4Si as internal standard. All NMR values are reported as chemical shift δ in ppm downfield from Me_4Si. Mass spectra were recorded on a V.G. Micromass 16F spectrometer. High resolution mass spectrometry was performed at the McMaster Regional Centre for Mass Spectrometry using a VG ZAB-E instrument in the EI mode at 70 eV. Elemental analyses were performed by Guelph Chemical Laboratories Limited. Preparative thin-layer chromatography (TLC) was carried out by using 20 × 20 cm glass plates coated with $^3/_4$ mm Merck silica gel (TLC grade). Indene and 9-fluorenecarboxylic acid were obtained from Aldrich and not further purified. 1-Indenecarboxylic acid was obtained by using a modified method as described by Noland.[20] Hydrogenation to indanecarboxylic acid was carried out on a Parr medium pressure hydrogenator at 60 psi pressure in ethanol.

Tetracyclic Ketone 7. 1-Indanecarboxylic acid chloride was prepared by heating a mixture of 1-indanecarboxylic (3.7 g) acid and thionyl chloride (6 mL) to reflux for 40 min. The excess $SOCl_2$ was evaporated and the residue consisting mainly of the acid chloride was not further purified. To a mixture of 2.3 g (1.27×10^{-2} mol) of the acid chloride and 2.22 g (2.78×10^{-2} mol) of 1,3-cyclohexadiene in 27 mL of dried benzene heated to 60 °C was added a solution of 1.30 g (1.28×10^{-2} mol) of triethylamine in 10 mL of benzene under a N_2 atmosphere. The solution was stirred under reflux for 1 h. After cooling, the precipitate was filtered off and the filtrate was washed with 200 mL of 10% HCl, 200 mL of 10% aqueous Na_2CO_3, and 200 mL of water, dried over $MgSO_4$, and concentrated. The solid material was recrystallized from ethanol and the mother liquor chromatographed on preparative TLC plates (benzene). The combined fractions yielded 2.83 g (99% yield) of white crystalline material, mp 88–89 °C: ^{1}H NMR δ 7.43–7.14 (4 H, m), 6.05 (1 H, m), 5.52 (1 H, m), 3.70 (1 H, m), 3.07 (2 H, m), 2.93 (1 H, m), 2.55 (1 H, m), 2.40 (1 H, m), 2.14 (3 H, m), 1.69 (1 H, m); IR (KBr) 1768 cm^{-1}; MS, *m/e* 224 (M^+), 144 ($M^+ - C_6H_8$, base peak). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.91; H, 7.30.

Pentacyclic Ketone 8. 9-Fluorenylcarboxylic acid chloride was prepared by heating a mixture of 10.9 g of 9-fluorenecarboxylic acid and 35 mL of thionyl chloride under reflux for 1 h. The excess $SOCl_2$ was evaporated and the acid chloride residue (IR: 1785 cm^{-1}) was used in the next step without further purification.

A solution of 5.0 g of the acid chloride and 40 mL of dry benzene was heated to 65 °C, whereupon 3.5 equiv of 1,3-cyclohexadiene was added, followed by 2.37 g (1 equiv) of triethylamine in 20 mL of benzene. The reaction was carried out under N_2. Addition of Et_3N caused an immediate formation of a white precipitate. The mixture was heated for 20 min. After filtering off the precipitate, the filtrate was washed with 10% HCl (4 × 50 mL), saturated $NaHCO_3$ (4 × 50 mL), and water (60 × 50 mL), dried over $MgSO_4$, and evaporated. The yellow solid was crystallized in methanol, giving 3.70 g of **8**, mp 154–155.5 °C: ^{1}H NMR δ 7.69 (2 H, d), 7.49–7.23 (6 H, m), 6.17 (1 H, m), 5.71 (1 H, m), 4.21 (1 H, m), 3.63 (1 H, m), 2.24 (3 H, m), 1.74 (1 H, m); MS, *m/e* 272 (M^+), 192 ($M^+ - C_6H_8$, base peak). Anal. Calcd for $C_{20}H_{16}O$: C, 88.24; H, 5.88. Found: C, 87.97; H, 6.23.

Acephenanthrylene (4). A solution of 2 g of ketone **7** in 10 mL of 50/50 ethanol/ether was added to 10 g of methanesulfonic acid at 5 °C with stirring under N_2. After addition the temperature was allowed to reach ambient and the reaction mixture was stirred for an additional 24 h. The mixture was poured onto ice/water and extracted with 200 mL of ether. The ether layer was washed with 3 × 20 ml saturated $NaHCO_3$ and then with the same amount of water, dried over $MgSO_4$, and evaporated to give an oily residue which consisted of two components by TLC. This was applied to 10 TLC plates and the bands separated by using 20% benzene/hexane mixture. The nonpolar fraction containing **9** (0.630 g) was not purified further but used for the next step: MS, *m/e* 206 (M^+); ^{1}H NMR δ 8.1 (1 H, d) 7.6 (1 H, t), 7.1–7.3 (2 H, m), 6.2 (1 H, d), 5.0 (1 H, d × t), 3.1 (2 H, m), 2.4 (4 H, m), 1.9 (2 H, m).

A solution of 0.50 g of **9** and 1.6 g of DDQ in 30 mL of benzene was heated under reflux for 2 h. The solvent was evaporated and the residue chromatographed on a column of alumina (10% benzene/hexane). The nonpolar fraction consisted of a slightly yellow crystalline compound **4** (0.25 g): mp 142–144 °C (lit.[15] mp 143–144 °C); ^{1}H NMR δ 8.30 (1 H, m), 8.0–7.0 (9 H, m); UV λ_{max} 360, 340, 325, 320, 300, 287, 270, 260, 255, 235, 227 nm.

The second more polar band from the reaction of **7** with acid was identified as ketone **10** (0.45 g): IR (thin film) 1700 cm^{-1}; ^{1}H NMR δ 7.0, 7.4 (3 H, m), 6.1 (1 H, d × d), 4.9 (1 H, m), 4.2 (1 H, m), 3.3–2.8 (2 H, m), 2.7–2.0 (6 H, m), 1.8 (2 H, m); MS, *m/e* 224 (M^+), 196 ($M^+ - CO$).

Reduction of ketone **10** was carried out by dissolved 0.4 g of **10** in 10 mL of anhydrous ether. This solution was added to a slurry of 0.1 g of LAH in 10 mL of ether and stirred at room temperature for 1 h. The excess LAH was quenched by using 0.1 mL of H_2O followed by addition of 0.1 mL of 15% NaOH and 0.3 mL of H_2O. After filtration, the filtrate was washed to neutrality with water dried over $MgSO_4$ and evaporated, giving 0.37 g of an oily residue; IR 3550 cm^{-1} (OH). The residue was dissolved in benzene and 1.5 g of DDQ was added. The solution was heated to reflux. After cooling, the solvent was evaporated and the residue chromatographed on an alumina column (10% benzene/hexane). A crystalline fraction (0.11 g) of **4** was obtained identical in all respects with the sample prepared from dehydrogenation of **9** as described before.

Tetracyclic Ketone 11. A solution containing 2.5 g (1.12×10^{-2} mol) of ketone **7** and 0.1 g of 5% Pd/C in 30 mL of absolute ethanol was hydrogenated in a Parr hydrogenator at 60 psi H_2 over a 24-h period. The solvent was evaporated to give 2.5 g of crystalline **11** which was recrystallized from ethanol: mp 52–53 °C; ^{1}H NMR δ 7.4–7.1 (4 H, m), 3.5 (1 H, t), 3.1–2.9 (1 H, m), 2.8–2.7 (1 H, m), 2.5–2.4 (2 H, m), 2.28–2.20 (1 H, m), 2.1–2.0 (1 H, m), 1.6–1.3 (4 H, m), 1.3–1.0 (3 H, m); MS, *m/e* 226 (M^+), 198 ($M^+ - CO$, base peak), 144 ($M^+ - C_6H_{10}$); IR 1770 cm^{-1} (C=O);

(18) Lee-Ruff, E.; Chung, Y. S., unpublished results.
(19) Hopkinson, A. C.; Lee-Ruff, E.; Maleki, M. *Synthesis* **1986**, *5*, 366.
(20) Noland, W. E.; Landucci, L. L.; Kameswaran, V. *J. Org. Chem.* **1980**, *45*, 3456.

Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H,8.02. Found: C, 84.51; H, 8.34.

2-(1-Indanyl)cyclohexancarboxylic Acid (12). A solution of ketone **11** (3.25 g, 1.44×10^{-2} mol) and KOH (1.3 g, 2.32×10^{-2} mol) in 30 mL of 90% EtOH and 15 mL of ether was heated under reflux for 24 h. The solvent was evaporated and 20 mL of ether and 50 mL of H_2O were added. The ether solution was washed with saturated Na_2CO_3 and the aqueous were washings combined. The aqueous layer was acidified with concentrated HCl. The acidified solution was re-extracted with 3 × 30 mL of ether. The ether extracts were dried over $MgSO_4$ and evaporated to give 3.37 g (1.38×10^{-2} mol) of yellow oil **12**: IR 1708cm^{-1}(C= O); ^{1}H NMR δ 1.0 (1H broad m), 7.5 - 7.1 (4H,m), 3.4 (1 H, m), 3.0–2.7 (3 H, m), 2.4–1.1 (11 H, m); MS, *m/e* 244 (M^+), 198 ($M^+ - CH_2O_2$), 117 ($M^+ - C_7H_{11}$, base peak).

Tetracyclic Ketone 13. To a Teflon reaction vessel was added 1.32 g (5.4×10^{-3} mol) of carboxylic acid **12**, and the vessel was cooled to −75 °C (2-propanol/dry ice). To this was added 10 mL of liquid HF while the mixture was stirred. After 30 min, the dry ice bath was replaced with an ice-water bath and the reaction was stirred overnight while the reaction mixture was slowly brought to ambient temperature. The reaction mixture was passed through a short neutral alumina column. Elution with benzene gave 1.2 g (5.31×10^{-3} mol) of white crystalline **13** (recrystallized EtOH), mp 130–132 °C: ^{1}H NMR δ 7.7 (1 H, d), 7.4 (1 H, d), 7.2 (1 H, t), 3.1–2.9 (3 H, m), 2.5–2.4 (2 H, m), 2.2 (1 H, d × t), 2.0 (1 H, m), 1.9 (1 H, m), 1.8 (1 H, m), 1.6 (2 H, m), 1.4–1.1 (4 H, m); IR 1680 cm^{-1} (C=O); MS, *m/e* 226 (M^+, base peak), 144 ($M^+ - C_6H_{10}$). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.83; H, 8.27.

Reduction of Ketone 13 with LAH. A solution of 1.1 g of ketone **13** in 90 mL of anhydrous ether was added to a slurry of 0.24 g (6.32×10^{-3} mol) of LAH in 30 mL of ether under N_2. The reaction mixture was stirred for 2 h. The reaction was quenched by the successive additions of 0.24 mL of H_2O, 0.24 mL of 15% NaOH, and 0.72 mL of H_2O. The solution was filtered, washed with water, and evaporated to give 1.07 g of white solid, mp 103–105 °C; IR (KBr) 3310 cm^{-1} (OH); ^{1}H NMR δ 7.2 (3 H, m), 4.9 (1 H, s), 3.1 (1 H, m), 2.8 (2 H, m), 2.1–1.7 (8 H, m), 1.6–1.3 (4 H, m), 1.2–1.0 (1 H, d × q); MS, *m/e* 228 (M^+), 210 ($M^+ - H_2O$), 146 ($M^+ - C_6H_{10}$). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.18; H, 9.12.

Hydrocarbons 14 and 15. A solution of 0.01 g of TsOH and 0.7 g of alcohol derived from ketone **13** in 25 mL of benzene was heated to reflux for 40 min. After cooling, the reaction mixture was poured over ice/water. The organic layer was separated, dried over $MgSO_4$, and evaporated to give a residue which was chromatographed on preparative TLC plates (hexane). Two crystalline nonpolar fractions were obtained, **14** (0.14 g) and **15** (0.175 g). Decreasing the reflux time to 10 min resulted in a 60% yield of **14** with no **15** detected. Also, substituting concentrated H_2SO_4 (4 mL) for TsOH and refluxing for 6 min gave **14** in 94% yield.

Hydrocarbon 14: mp 68–70 °C; ^{1}H NMR δ 7.3 (1 H, d), 7.1 (1 H, t), 7.0 (1 H, d), 6.0 (1 H, d), 3.4 (2 H, d), 2.8–2.5 (2 H, m), 2.4–2.2 (2 H, m), 2.0–1.8 (3 H, m), 1.6–1.2 (5 H, m); MS, *m/e* 210 (M^+, base peak), 128 ($M^+ - C_6H_{10}$). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.41; H, 8.67.

Hydrocarbon 15: mp 43–44 °C; ^{1}H NMR δ 7.5 (1 H, d), 7.4–7.3 (2 H,m), 7.14 (1 H, d), 3.4–3.3 (2 H, m), 3.2–3.1 (2 H, m), 3.0 (2 H, t), 2.8 (2 H, t), 1.9–1.8 (4 H, m); MS, *m/e* 208 (M^+, base peak); UV λ_{max} (nm, ϵ 10^{-4}), 298 (0.3), 288 (0.28), 236 (9.53).

Aceanthrylene (1). A mixture of 0.047 g (0.22×10^{-3} mol) of **14** and 0.2 g (0.89×10^{-3} mol) of DDQ in 1 mL of dry benzene was heated to reflux for 30 min. After cooling, the solution was filtered and evaporated to give a residue which was applied to a column of basic alumina. Elution with benzene gave a reddish solid which was sublimed in vacuo (5×10^{-3} torr). A yellowish crytalline material was collected (0.005 g), identified as **1**; mp 103–104.5 °C (lit.[7] mp 103–104 °C); ^{1}H NMR δ 8.5 (1 H, s), 8.3 (1 H, d), 8.1 (1 H, d), 8.0 (1 H, d), 7.8 (1 H, d), 7.6–7.55 (3 H, m), 7.5 (1 H, t), 7.1 (1 H, d); MS, *m/e* 202 (M^+, base peak); UV λ (nm) 400, 384, 362, 346, 256, 238. All of the above spectral data were identical with those of an authentic sample.[16]

Acid Rearrangement of Pentacyclic Ketone 8. Ketone **8** (1.4 g) was dissolved in 30 mL of chloroform and the solution was added dropwise to a cooled (ice/water) solution of 20 mL of methanesulfonic acid and 1 mL of chloroform under N_2. The yellow solution turned orange and then dark red. After being stirred at 0 °C for 4.5 h, the reaction mixture was poured onto crushed ice. The aqueous layer was extracted with chloroform (3 × 40 mL). The combined chloroform extracts were washed with saturated $NaHCO_3$ (3 × 40 mL) and water (3 × 40 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to yield 1.3 g of an oily residue. This was applied to silica gel column and eluted with a 1:1 mixture of hexane and chloromethane. A fraction (820 mg) was collected consisting of several overlapping components representing stereoisomers of **16**. Fluorenone (100 mg) was also obtained. The major fraction had the followed spectral characteristics: IR (thin film) 1710 cm^1 (C=O); ^{1}H NMR δ 7.81 (d), 7.75–7.78 (m), 7.69 (d), 7.55 (d), 7.22–7.43 (m), 7.18 (d), 6.70 (s), 6.15–6.25 (m), 5.97–6.05 (m), 4.35 (s), 2.72–2.81 (m), 2.52–2.68 (m), 2.25–2.37 (m), 1.98–2.21 (m), 1.74–1.92 (m), 1.06–1.16 (m), 0.78–0.94 (m), 0.37–0.56 (m); MS, *m/e* 272 (M^+), 244 (M^+ - CO); high resolution MS, *m/e* calcd 272.1201, found 272.1201.

Tetrahydrobenz[*e*]acephenanthrylene (17) (Mixture of Regioisomers). To a cooled solution (0 °C) of 0.285 g of ketone **16** (stereoisomeric mixture) in 25 mL of distilled THF was added a suspension of 0.5 g of LAH in 40 mL of THF. The mixture was stirred at 0 °C for 4 h under N_2. To this solution was added in the following sequence 0.5 mL of H_2O, 0.5 mL of a 15% NaOH solution, and 1.5 mL of water. The precipitate was filtered and washed with THF. The filtrate was evaporated under reduced pressure to give 0.265 g of a yellow solid; IR 3200–3650 cm^{-1} (OH). The crude alcohol was dissolved in 20 g of PPA heated to 130 °C for 30 min. The brown viscous solution was poured over 200 mL of water. The solution was extracted with 3 × 40 mL of chloroform and the combined chloroform extracts washed with 3 × 40 mL of water, dried over anhydrous $MgSO_4$, filtered, and evaporated, giving a brown oil. The crude mixture was applied to silical gel plates ($^3/_4$ mm) and eluted with hexane, giving a nonpolar fraction consisting of 0.15 g of **17** and a regioisomer which could not be separated: ^{1}H NMR δ 8.68 (d), 8.48 (d), 8.25 (s), 7.28–8.10 (m), 6.33 (m), 5.96 (m), 5.53 (s), 4.10–4.30 (m), 1.7–3.1 (m); MS, *m/e* 256 (M^+), 252 (M^+ - 4 H), 165; high resolution MS, *m/e* calcd 256.1252, found 256.1235.

Benz[*e*]acephenanthrylene. A solution containing 0.06 g of **17**, 25 mL of dry benzene, and 0.185 g of DDQ was heated under reflux for 2.75 h. After cooling the solution to room temperature, the product was adsorbed on to silica gel. The adsorbed product was placed on top of a silica gel column and eluted with benzene. The major fraction was further purified by preparative TLC, developing the plates with hexane to give 0.044 g of white crystalline solid, mp 168–169.5 °C (lit.[21] mp 168); UV λ_{max} (EtOH) 222, 255, 277, 290, 301; ^{1}H NMR δ 8.62 (d, 1 H), 8.41 (d, 1 H), 8.16 (s, 1 H), 7.90–8.02 (m, 4 H), 7.59–7.75 (m, 3 H), 7.40–7.45 (m, 2 H); MS, *m/e* (relative intensity) 252 (M^+, 100), 250 (28), 126 (34); high resolution MS, *m/e* calcd 252.0939, found 252.0923.

Tetracyclic Alcohol 18. To 1 g of ketone **8** in 100 mL of absolute ethanol and 50 mL of dry THF was added 1 g of $NaBH_4$, and the mixture stirred at room temperature for 3 h. This was quenched with 200 mL of water and extracted with 3 × 30 mL of chloroform. The combined chloroform extracts were washed with 3 × 40 mL of water, dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was adsorbed onto silica gel and passed through a silica gel column by elution with CH_2Cl_2/hexane (1:1), giving 0.56 g of oil **18** and 0.18 g of fluorenone. The spectral data for **18** are as follows: IR 3170–3560 cm^{-1} (OH); ^{1}H NMR δ 7.68–7.83 (m, 3 H), 7.54 (d, 1 H), 7.25–7.41 (m, 3 H), 7.22 (t, 1 H), 6.05 (d, 1 H), 5.92 (m, 1 H), 4.10–4.20 (s, 1 H), 3.43–3.53 (s, 1 H), 2.85 (t, 1 H), 2.59–2.70 (m, 1 H), 2.00–2.20 (s, 2 H), 1.85–2.00 (m, 1 H), 1.40–1.65 (m, 2 H), 0.73–0.82 (s, exchangeable with D_2O); MS, *m/e* (relative intensity) 276 (M^+, 13), 165 (100), 111 (13), 93 (30), 84 (36); high resolution MS, *m/e* calcd 276.1514, found 276.1527.

Tetrahydrobenz[*a*]aceanthrylene (19). Alcohol **18** (0.2 g) was placed in a Teflon bottle and cooled to −78 °C using a 2-propanol/dry ice bath. About 20 mL of liquid HF was then added, resulting in the formation of a red solution. After 10 min, the

(21) Clar, E. *Polycylic Hydrocarbons*; Academic Press: New York, 1964; Vol. 2.

2-propanol bath was replaced with an ice/water bath and stirred for another 5 h. The cap of the Teflon bottle was removed to allow HF to slowly evaporate. The residue was adsorbed onto silica gel, placed on top of a silica gel column, and eluted with a hexane/benzene mixture (80:20), yielding 0.12 g of a yellow solid which was recrystallized from methanol, mp 80–81 °C: ^{1}H NMR δ 7.91–7.97 (m, 2 H), 7.87 (d, 1 H), 7.73 (d, 1 H), 7.50–7.58 (m, 2 H), 7.34–7.39 (m, 2 H), 3.46 (t, 2 H), 3.10 (t, 2 H), 1.99–2.10 (m, 2 H), 1.88–1.99 (m, 2 H); MS, *m/e* (relative intensity) 256 (M^+, 100), 254 (23), 228 (36), 226 (22); high resolution MS, *m/e* calcd 256.1252, found 256.1247.

Benz[*a*]aceanthrylene (5). Hydrocarbon **19** (0.3 g) was dissolved in 60 mL of dry benzene. To this solution was added 0.7 g of DDQ and the mixture was refluxed for 2 h. The solution was allowed to cool and adsorbed onto silica gel, placed on top of a silica gel column, and eluted with benzene. The nonpolar fraction was applied to preparative TLC plates (1 mm) and developed with a hexane/benzene mixture (4:1). The major component was crystallized from ethanol, giving 0.23 g of yellow crytalline needles; mp 144.5–146 °C (lit.[21] mp 145–146 °C); UV λ_{max} (EtOH) 215, 258; ^{1}H NMR δ 7.36–7.52 (m, 3 H), 7.60–7.67 (m, 2 H), 7.96–8.00 (m, 3 H), 8.11 (d, 1 H), 8.36 (d, 1 H), 8.42 (s, 1 H), 8.72 (d, 1 H); MS, *m/e* (relative intensity) 252 (M^+, 100), 249 (41), 125 (18), 113 (11); high resolution MS, *m/e* calcd 252.0939, found 252.0927.

Acknowledgment. We gratefully acknowledge the generous financial support of this work by the Natural Science and Engineering Research Council of Canada, as well as the Ontario Ministry of Environment ARB.

The Structure of the Products from the Reaction of 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione with Alcohols

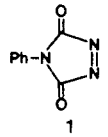
Donald Mackay,* Nicholas J. Taylor, and Ian D. Wigle

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Waterloo, Ontario, Canada N2L 3G1

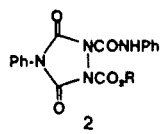
Received August 11, 1986

The title azo compound (**1**) reacts with alcohols to give 1-(alkoxycarbonyl)-2-(*N*-phenylcarbamoyl)-4-phenyl-1,2,4-triazolidine-3,5-diones (**2**), the structures originally assigned to them. The X-ray diffraction analysis of the butyl compound **2c** is described, together with details of its synthesis from **1** and from the parent urazole **7**.

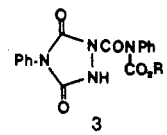
Ten years ago in a preliminary communication[1] and later in a full paper,[2] we described the formation of 1-(alkoxycarbonyl)-2-(*N*-phenylcarbamoyl)-4-phenyl-1,2,4-triazolidine-3,5-diones (**2**) from the interaction of two molecules of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**) and one of alcohol, with the loss of one molecule of nitrogen. An independent synthesis of one of these, the methyl ester **2a**, was also reported.[2]



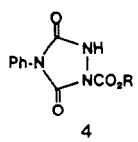
1



2



3

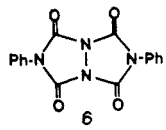


4

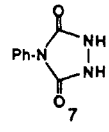
PhNHCO$_2$R

5

a R = Me
b R = Et
c R = n-Bu
d R = i-Pr
e R = c-C$_5$H$_9$
f R = CH$_2$Ph



6



7

Table I. Selected X-ray Crystallographic Parameters for 2c

bond lengths, Å		bond angles, deg		Σ^a
N(1)–N(2)	1.407 (3)	N(2)–N(1)–C(5)	108.4 (2)	
N(1)–C(5)	1.408 (4)	N(2)–N(1)–C(6)	115.1 (2)	348.2 (4)
N(1)–C(6)	1.427 (5)	C(5)–N(1)–C(6)	124.7 (2)	
N(2)–C(3)	1.395 (5)			
N(2)–C(13)	1.457 (4)	N(1)–N(2)–C(3)	108.7 (2)	
C(3)–N(4)	1.389 (4)	N(1)–N(2)–C(13)	114.0 (2)	346.8 (4)
C(3)–O(22)	1.197 (4)	C(3)–N(2)–C(13)	124.1 (2)	
N(4)–C(5)	1.383 (5)			
N(4)–C(23)	1.429 (5)	C(3)–N(4)–C(5)	112.1 (2)	
C(5)–O(29)	1.199 (3)	C(3)–N(4)–C(23)	124.1 (2)	359.8 (4)
		C(5)–N(4)–C(23)	123.6 (2)	

[a] The sum of bond angles about each of the three nitrogens in the heterocyclic ring is included to show the degree of nonplanarity at N(1) and N(2).

A recent publication describing the reactions of **1** with a variety of solvents, including alcohols, implicitly questions our findings.[3] Compounds **2** were not isolated. Structural isomers of **2**, the 1-[*N*-phenyl-*N*-(alkoxycarbonyl)carbamoyl]-4-phenyl-1,2,4-triazolidine-3,5-diones (**3**), were postulated as reactive intermediates, which with excess of alcohol were presumed to give the alkoxycarbonyl derivatives **4** and the urethanes **5**, products isolated from the reactions. From the decomposition of **1** with equimolar methanol, repeated crystallization of the reaction residues gave a small amount (2%) of a compound $C_{17}H_{14}N_4O_5$ to which structure **3a** was assigned. IR, ^{1}H NMR, and MS data were obtained, but insufficient material was available to study its reactivity.

(1) Dao, L. H.; Mackay, D. *J. Chem. Soc., Chem. Commun.* **1976**, 326.
(2) Dao, L. H.; Mackay, D. *Can. J. Chem.* **1979**, *57*, 2727.
(3) Izydore, R. A.; Johnson, H. E.; Horton, R. T. *J. Org. Chem.* **1985**, *50*, 4589.

0022-3263/87/1952-1288$01.50/0