an inverted gas buret via a dry ice vapor trap. The side arm of the flask was fitted with a silicon rubber stopple. The flask was cooled in a dry nitrogen atmosphere. The reaction flask was immersed in a water bath at room temperature (ca. 25 °C). THF (24.7 mL) was introduced into the reaction flask, followed by 5.3 mL (10 mmol) of 1.89 M lithium aluminum hydride solution. Finally, 10 mL (10 mmol) of 1.0 M solution of *n*-butyl bromide in THF was introduced. The reaction mixture was stirred vigorously and the hydrogen evolved was measured. Simultaneously, a blank was run in which, instead of the 10 mL of alkyl bromide solution, 10 mL of tetrahydrofuran was added, all other conditions being the same.

After 15 min, 0.02 mmol of hydrogen had evolved per millimole of the halide. Now a 4.0-mL aliquot of the reaction mixture (1.0 mmol of halide) was removed with a hypodermic syringe and injected into a hydrolyzing mixture of 1:1 glycerine–water in tetrahydrofuran. The hydrogen evolved was measured by a gas buret. Immediately, 4.0 mL of the blank was also taken out and hydrolyzed and the hydrogen evolved was measured. The difference between the blank value and the reaction mixture in millimoles gives the amount of hydride used by 1 mmol of the compound. This revealed that 0.78 mmol of hydride had been utilized by 1 mmol of the halide for reduction in 15 min. In other words, 78% reduction had occurred. The reduction was complete in 1 h.

In general, the hydrogen evolution measurement, and the hydrolysis of the reaction mixture were done at 0.25, 0.5, 1, 3, 6, 12, and 24 h. The results for other alkyl halides are summarized in Table I.

In most cases, the hydrogen evolution from the reaction mixture was negligible, indicating that no β elimination occurred. The hydrogen evolved from the reaction mixture is an approximate measure of β elimination.

Procedure for Product Analysis. For establishment of the reaction products, separate reductions on a 5-mmol scale were carried out. Most of the reductions were carried out under standard conditions. In a few cases, the temperature or both the temperature and the concentration of lithium aluminum hydride had to be increased in order to decrease the reaction time. Analyses were carried out by gas chromatography, using a suitable internal standard. The reaction mixture was analyzed for the alkane, alkene (if any present), and the remaining halide (Table II).

The reductions of *n*-octyl bromide and cyclohexyl iodide are representative.

***n*-Octyl Bromide.** A clean, dry 100-mL flask, oven-dried, equipped with a side arm fitted with a silicon rubber stopple, a magnetic stirring bar, and reflux condenser connected to a mercury bubbler, was cooled with nitrogen. The reaction flask was immersed in a water bath (ca. 25 °C). Then 5 mL of tetrahydrofuran was injected into the reaction flask by a hypodermic syringe, followed by 5 mL (5 mmol) of 1.0 M solution of lithium aluminum hydride and 5 mmol of *n*-nonane (in 5 mL of THF) as internal standard. Finally, 5 mmol of *n*-octyl bromide (in 5 mL of THF) was injected. The reaction mixture was 0.25 M in both $LiAlH_4$ and bromide. The reaction mixture was stirred well. GLC analysis of the reaction mixture after 5 min indicated that 70% of the reduction had occurred. After 30 min, excess hydride was destroyed by slowly adding a 1:1 mixture of tetrahydrofuran–water dropwise through a hypodermic syringe. Then 3 mL of a saturated solution of sodium potassium tartrate was added to complex aluminum salts. After the mixture was dried, the ethereal layer was subjected to gas chromatographic examination on column A. The analysis revealed the presence of 96% *n*-octane and only 1–2% of *n*-octyl bromide. Analysis of the reaction mixture on column D indicated the absence of any olefin, 1-octene.

Cyclohexyl Iodide. The experimental setup was the same as in the previous experiment. Five milliliters of tetrahydrofuran was introduced into the reaction flask, followed by 5 mL (5 mmol) of 1.0 M lithium aluminum hydride solution and 5 mmol of toluene in 5 mL of THF in the order indicated. The reaction flask was heated carefully to reflux temperature. Then 5 mmol of cyclohexyl iodide (in 5 mL of THF) was introduced by a syringe. The reaction mixture was stirred well with a magnetic stirrer. After 6 h, heating was stopped and the reaction flask was cooled in an ice bath. Excess hydride was destroyed by adding a 1:1 mixture of tetrahydrofuran and water through a syringe. The condenser was washed with THF, and the washings were collected in the reaction flask so as to recover any volatile products from the condenser surface. Aluminum salts were complexed with a saturated solution of sodium potassium tartrate. The THF layer was dried with anhydrous Na_2SO_4. A standard authentic synthetic mixture was also prepared under identical conditions, as follows. Equimolar amounts of cyclohexane, cyclohexene, toluene, and lithium aluminum hydride were heated at reflux for 6 h and worked up exactly as the reaction mixture. Gas chromatographic examination on column C revealed the presence of 93% cyclohexane and less than 1% of cyclohexene and cyclohexyl iodide.

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Registry No. *n*-Butyl iodide, 542-69-8; *n*-butyl bromide, 109-65-9; *n*-butyl chloride, 109-69-3; *sec*-butyl bromide, 78-76-2; *tert*-butyl bromide, 507-19-7; isobutyl bromide, 78-77-3; 1-bromo-2-methylpentane, 25346-33-2; neopentyl bromide, 630-17-1; β-bromostyrene, 103-64-0; bromobenzene, 108-86-1; 1-bromonaphthalene, 90-11-9; benzyl bromide, 100-39-0; allyl bromide, 106-95-6; cyclopentyl bromide, 137-43-9; cyclohexyl bromide, 108-85-0; cycloheptyl bromide, 2404-35-5; cyclooctyl bromide, 1556-09-8; cyclohexyl iodide, 626-62-0; cyclohexyl chloride, 542-18-7; *exo*-2-bromonorbornane, 2534-77-2; *endo*-2-bromonorbornane, 13237-87-1; 1-iodooctane, 629-27-6; 1-bromooctane, 111-83-1; 1-chlorooctane, 111-85-3; 2-bromooctane, 557-35-7; lithium aluminum hydride, 16853-85-3.

Reactions of Spiro[fluorenetriazolines]

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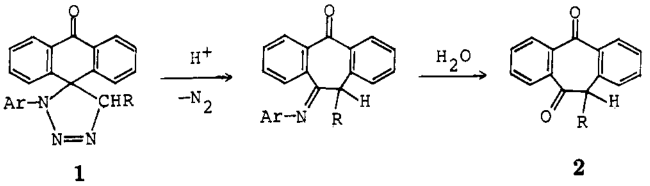
Methylenefluorene **3a** adds regiospecifically to aryl azides **4** to give the corresponding spiro[fluorenetriazolines] **5**, which lead to the ring-enlargement products, 9-(arylamino)phenanthrenes (**9**), by pyrolysis and acid-induced reaction. Benzylidenefluorene **3b** reacts with **4** to give 9-(arylamino)-10-phenylphenanthrenes (**10**), instead of spirotriazolines.

We have previously investigated the reactions of quinone methides with aryl azides and the ring-enlargement reactions of the main products, spiro[anthronetriazolines] **1**, to dibenzo[*a*,*d*]cycloheptenedienes **2**.[1] This work has now



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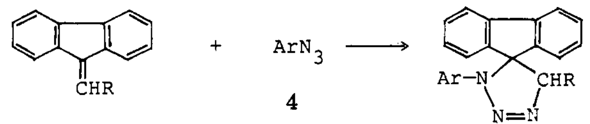
2

been extended to the reactions of spiro[fluorenetriazolines], containing both a fluorene moiety and a triazoline ring in a spiro configuration, to see whether these compounds behave like 1 in the ring-enlargement reaction. This heterocyclic system is also expected to be highly reactive because of the possibility that reactive intermediates are obtained from it by loss of nitrogen. We have, therefore, examined the acid-induced reactions, pyrolysis, and photolysis of the spiro[fluorenetriazolines] from reactions of methylenefluorenes 3 with aryl azides 4 and their utilization in the preparations of phenanthrenes.

Results and Discussion

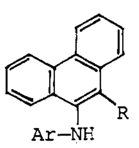
Reactions of Methylenefluorenes with Aryl Azides. Reaction of 9-methylenefluorene (**3a**) with an excess of aryl azides **4a–d** at 90 °C gave the corresponding spiro[fluorenetriazolines] **5a–d** in 25–56% yields (Table I). However, the reaction with **4e** gave no spirotriazoline but rather 9-[(4-nitrophenyl)amino]phenanthrene (**9e**). The polymer[2] of **3a** was obtained in all runs in ca. 40% yields. In the cycloaddition, **3a** reacts with **4** in a regiospecific manner to give exclusively **5** or products obtained by further rearrangement and/or reactions of **5**. The homogeneity and gross structure of **5** are supported by ^{1}H NMR spectra which show a sharp singlet methylene absorption at ca. δ 4.8–4.9. Alternate regioisomer **6** which would result from the alternate mode of cycloaddition was not detected in any of the adducts. The assignments of the spirotriazolines as **5** rather than as its regioisomer **6** were based on the observation that the reaction of spirotriazolines with acid catalyst gave the ring-enlargement products, 9-(arylamino)phenanthrenes (**9**), in good yields (see below).[1,3]



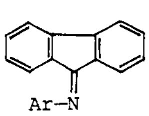
3a, R = H
b, R = Ph

4

5, R = H
7, R = Ph



9, R = H
10, R = Ph



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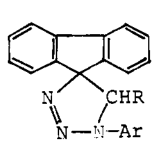

6, R = H
8, R = Ph

a, Ar = Ph; b, Ar = 4-MeC$_6$H$_4$; c, Ar = 4-MeOC$_6$H$_4$; d, Ar = 4-ClC$_6$H$_4$; e, Ar = 4-NO$_2$C$_6$H$_4$

Table I. Reactions of Methylenefluorenes 3 with Aryl Azides 4

	product yield, %		
reactants	5	9	polymer of 3a[2]
3a, 4a	32	0	38
3a, 4b	25	0	37
3a, 4c	25	0	39
3a, 4d	56	0	39
3a, 4e	0	37	42
	product yield, %		
reactants	7	10	11
3b, 4a	0	60	0
3b, 4b	0	40	0
3b, 4c	0	52	35
3b, 4d	0	36	0
3b, 4e	0	66	0

9-Benzylidenefluorene (**3b**) reacted with **4** to give 9-(arylamino)-10-phenylphenanthrenes (**10**) in 32–55% yields, as shown in Table I. In these reactions, the expected spirotriazolines **7** and **8** were not isolated. The reaction with **4c** afforded the (arylimino)fluorene **11c** (35%) in addition to **10c**.

The structures of **9e** and **10a–e** were confirmed by their analytical and spectral data (ν_{NH} ca. 3400 cm^{-1}). The (arylamino)fluorene **11c** was identified by comparison with a sample prepared independently by the reaction of fluorene with 4-methoxyaniline in the presence of zinc chloride. The compounds **9e**, **10a–e**, and **11c** probably arise from a secondary pyrolysis of the corresponding **5** and **7** which are thermally unstable.

Acid-Induced Reaction of Spiro[fluorenetriazolines]. In agreement with the earlier findings,[1] treatment of **5a–d** with hydrochloric acid in acetone resulted in rapid evolution of nitrogen and formation of the corresponding **9** (85–89%, Table II). A conceivable mechanism for this acid-induced reaction is shown in Scheme I. Protonation of the triazoline nitrogen produces diazonium ion **12**, the role of the basic site being evident from the comparable behavior of Δ^2-1,2,3-triazolines and 1-pyrazolines (on treatment with acid, no nitrogen loss from 1-pyrazolines is observed),[4] and then **12** rearranges with loss of nitrogen to **13**;[3a] deprotonation of **13** leads to **14**, which subsequently isomerizes to **9**. This process is analogous to that for the ring-enlargement reactions of **1** to **2**,[1] triazaspiro[4.5]decenes to cycloheptanones,[3a] and triazadispiro[2.0.5.3]dodecenes to spirononanones.[3a,5] In the cases of the acid-induced reaction of these heterocycles, imine intermediates corresponding to **14** readily hydrolyze to give ketones.[1,3a] In contrast, the imine **14** leads to **9** because of aromatization of the 9,10-dihydrophenanthrene to the phenanthrene ring which is more stable.

If the spirotriazolines formed from **3a** and **4a–d** have alternate structures **6a–d** which would result from the

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(1) Hirakawa, K.; Ito, T.; Okubo, Y.; Nakazawa, S. *J. Org. Chem.* **1980**, *45*, 1668–1672.

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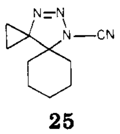
(4) (a) Scheiner, P. In "Selective Organic Transformations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 1, pp 327–362 and references cited therein. (b) Bianchi, G.; De Micheli, C.; Gandolfi, R. In "The Chemistry of Double Bonded Functional Groups"; Patai, S., Ed.; Wiley-Interscience: New York, 1977; Chapter 6 and references cited therein.

(5) In ref 3a, cyclopropylidenecyclohexane reacts with cyanogen azide, followed by hydrolysis, to afford two ring-enlargement cyclic ketones, spiro[2.6]nonan-4-one and spiro[3.5]nonan-1-one, in a 60:40 ratio. In this reaction, the intermediates are the triazoline regioisomers **25** and **26**, which, however, are not isolated.



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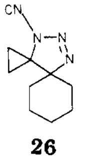

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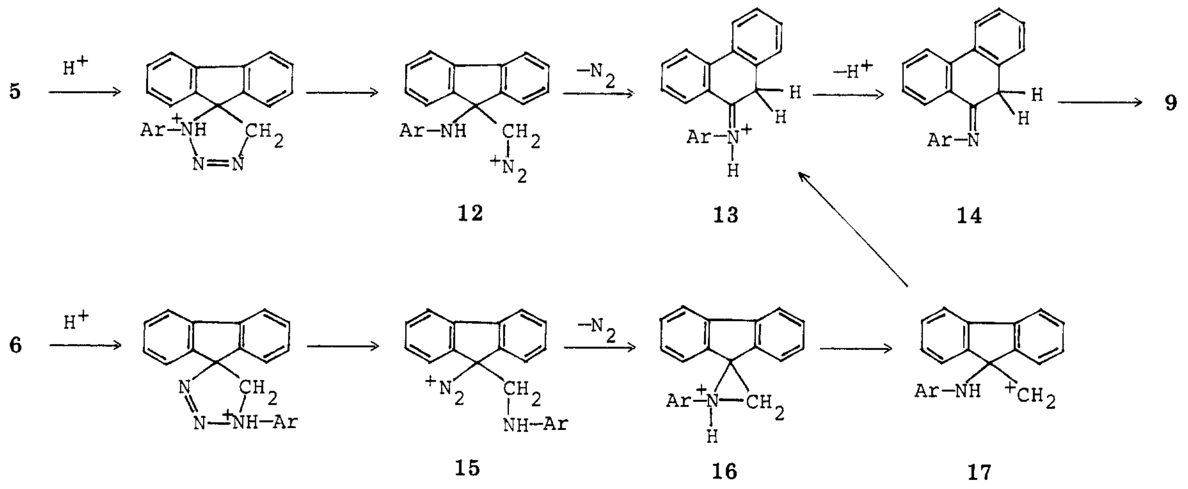
Scheme I



Scheme II

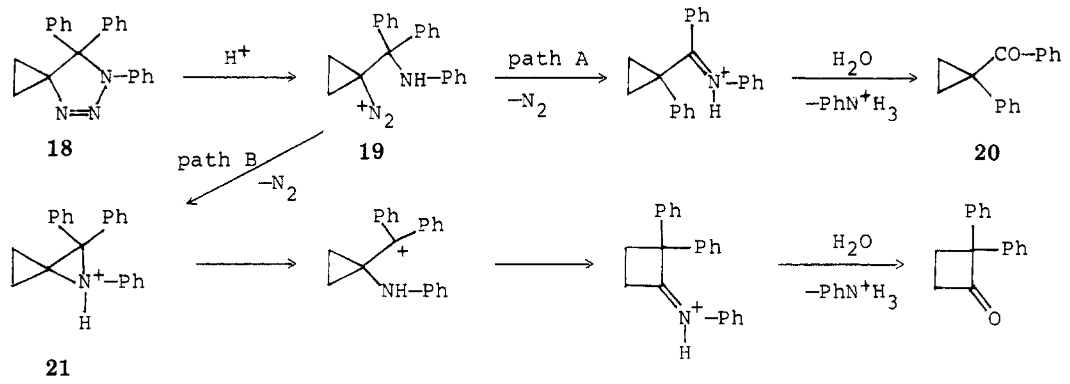


Table II. Reactions of Spiro[fluorenetriazolines] 5

triazoline	% yield of 9 acid-induced reaction		
	acid-induced reaction	pyrolysis	photolysis
5a	85	68	12
5b	89	69	15
5c	85	74	10
5d	87	75	trace

alternate mode of addition, their acid-induced ring enlargements have to proceed by an alternate path (**6** → **15** → **16** → **17** → **13** → **9**). The path of the diazonium ion **15** to the protonated spiroaziridine **16** may be unacceptable.[3a,4] Therefore, the structures of the spirotriazolines are **5a–d**. This argument for structural assignment is considerably strengthened by the fact that the acid-induced reaction of the spirotriazoline **18** (the substituent-bearing nitrogen of phenyl azide bonds to the spiro carbon), as expected, led to 1-benzoyl-1-phenylcyclopropane (**20**, 97%); i.e., the reaction may be satisfactorily explained on the basis of the path A involving the formation of diazonium ion **19** (Scheme II). If path B involves the formation of the protonated spiroazirizine **21**, one would expect 2,2-diphenylcyclobutanone rather than **20** to be formed.[3c]

Pyrolysis and Photolysis of Spiro[fluorenetriazolines]. In general, thermal decomposition of Δ^2-1,2,3-triazolines has given mixtures of imines and aziridines, and photodecomposition has afforded aziridines in high yields.[4a] However, heat treatment of the spirotriazolines **5a–d** in refluxing xylene gave **9a–d**, respectively, in 68–75% yields (Table II). The formation of **9** can be accounted for by the path involving the formation of diazonium zwitterionic intermediate **22**, followed by its thermal rearrangement with loss of nitrogen (Scheme III).[1,4,6] Although the aziridine appears to be a potential intermediate,[3b,c] its participation may not be required to explain the above results.[4] Similarly, it seems reasonable that in the reaction of **3b** with **4** the products **10** and **11** were formed by the path involving the formation of **7**, followed by its thermal rearrangement and fragmentation via diazonium zwitterionic intermediates **23**.

Irradiation of **5** in benzene gave **9** (~15%) and a complex mixture of products; the spiroaziridines were not obtained. The photolytic formation of **9** is explained by the rearrangement of the biradical **24** arising from **5**.[4a]

Finally, the acid-induced and thermal ring-enlargement reactions of the spiro[fluorenetriazolines] are available as a synthetic route to phenanthrenes.[7] The reactions generally go in good yields, and there are no byproducts to hinder isolation.

Experimental Section

Melting points were determined with a Yanagimoto hot-stage apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer Model 240 elemental analyzer. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer (KBr disk), ^{1}H NMR spectra on a JEOL JNM-3H-60 (60 MHz) spectrometer for solutions in deuteriochloroform (tetramethylsilane as the standard), and mass spectra on a JEOL JMS-01SG-2 spectrometer (at 75 eV). For analytical TLC, Wakogel B-10 (Wako Pure

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(6) Hermes, M. E.; Marsh, F. D. *J. Org. Chem.* **1972**, *37*, 2969–2979.

(7) Floyd, A. j.; Dyke, S. F.; Ward, S. D. *Chem. Rev.* **1976**, *76*, 509–562.

Scheme III

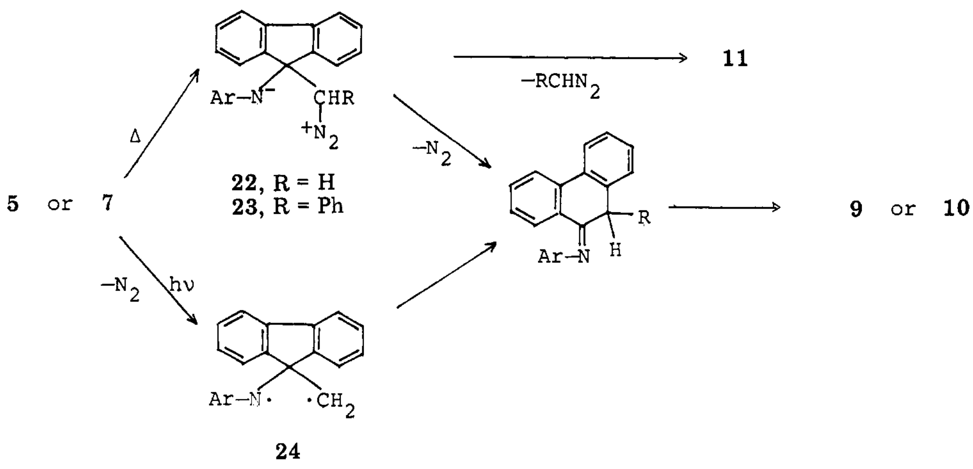

Table III. Melting Points of Compounds

compd	mp, °C	compd	mp, °C
5a	187-188 dec	9e	177-178
5b	195-196 dec	10a	169-171
5c	171-172	10b	244-246
5d	180-181 dec	10c	184-185
9a	136[a]	10d	227-228
9b	125	10e	196-197
9c	104	11c	137
9d	171		

[a] Lit.[13] mp 138 °C.

Chemical Industries) was used. Components were detected by staining with iodine vapor. Column chromatography was carried out with Wakogel C-200. Irradiations were carried out with an Ushio UM-102 100-W high-pressure mercury lamp through a Pyrex filter. Purity of products was checked by TLC and spectral analyses.

The following compounds were prepared according to previously known procedures: 9-methylenefluorene (**3a**),[8] 9-benzylidenefluorene (**3b**),[9] and aryl azides **4a–e**.[10]

Reaction of 3a with 4. A mixture of **3a** (1.78 g 10 mmol; freshly prepared) and **4** (30 mmol) was allowed to stand at 90 ± 2 °C for ca. 5 h, after which time **3a** had completely reacted upon ^{1}H NMR examination. The excess aryl azide was removed under reduced pressure, except that excess **4e** was removed by chromatography, and then the residue was extracted with benzene to remove the insoluble polymer[2] of **3a**. The extract was concentrated, and the residue was recrystallized from benzene-hexane to give the spiro[fluorenetriazoline] **5** or the 9-(arylamino)-phenanthrene **9**. Results and melting points of the products are summarized in Tables I and III, respectively. Spectral and analytical data of the representative product **5a** are given below. See the supplementary material for characterization data on the other products.[11]

1′-Phenylspiro[fluorene-9,5′-(1′,2′,3′-triazacyclopent-2′-ene)] (5a): colorless microcrystals; ^{1}H NMR δ 4.77 (s, 2 H, CH_2), 6.50–7.08 (m, 5 H, C_6H_5), 7.12–7.55 (m, 6 H, 1-, 2-, 3-, 6-, 7-, and 8-H), 7.55–7.78 (m, 2 H, 4- and 5-H); mass spectrum, *m/e* (relative intensity) 269 ($M^+ - 28$, 100), 268 (42), 267 (27), 165 (15). Anal. Calcd for $C_{20}H_{15}N_3$: C, 80.78; H, 5.09; N, 14.13. Found: C, 80.66; H, 5.10; N, 13.99.

Reaction of 3b with 4. A mixture of **3b** (2.54 g, 10 mmol) and **4** (30 mmol) was heated on a steam bath until TLC showed the absence of **3b** (50–60 h). Removal of the excess aryl azide by steam distillation left a residue which was extracted with chloroform, and extracts were dried and evaporated. Chromatography on silica [benzene–hexane (1:1) or benzene] gave 9-(arylamino)-10-phenylphenanthrene (**10**) and/or 9-(arylimino)fluorene (**11**). Results and melting points of the products are shown in Tables I and III, respectively. The spectral and analytical data of **10a** and **11c** are given below. See the supplementary material for data of **11b–e**.[11]

10-Phenyl-9-(phenylamino)phenanthrene (10a): pale yellow microcrystals (from benzene–hexane); R_f 0.38 (benzene–hexane, 1:1); IR 3375 cm^{-1} (NH); ^{1}H NMR δ 5.50 (br s, 1 H, NH), 6.40–8.30 (m, 16 H, aromatic H), 8.75–9.00 (m, 2 H, 4- and 5-H); mass spectrum *m/e* (relative intensity) 345 (M^+, 100), 267 (17), 254 (14), 253 (14), 252 (15), 165 (12). Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.06. Found: C, 90.21; H, 5.62; N, 3.98.

9-[(4-Methoxyphenyl)imino]fluorene (11c): yellow needles (from ethanol); R_f 0.55 (benzene); IR 1662 cm^{-1} (C=N); ^{1}H NMR δ 3.84 (s, 3 H, Me) and 6.55–7.95 (m, 12 H, aromatic H); mass spectrum, *m/e* (relative intensity) 285 (M^+, 82), 270 (100), 241 (32), 165 (15), 149 (17). Anal. Calcd for $C_{20}H_{15}NO$: C, 84.18; H, 5.30; N, 4.91. Found: C, 84.06; H, 5.38; N, 4.89.

The (arylimino)fluorene **11c** was prepared independently in a 65% yield from the reaction of fluorene with 4-methoxyaniline in the presence of zinc chloride.[12]

Reaction of 5 with Hydrochloric Acid in Acetone. A suspension of **5** (2 mmol) in acetone (20 mL) containing hydrochloric acid (0.2 mL) was stirred at room temperature until gas evolution ceased (~20 min), and then the resulting mixture was poured into water. The precipitate was collected and washed with water. Recrystallization from benzene–hexane gave **9** (Table II). The data for the representative products are given below. See the supplementary material for data on the other products.[11]

9-(Phenylamino)phenanthrene (9a): colorless microcrystals; identical with an authentic specimen.[13]

9-(4-Tolylamino)phenanthrene (9b): yellow microcrystals; IR 3054 cm^{-1} (NH); ^{1}H NMR δ 2.32 (s, 3 H, Me), 7.09 (AB q, 4 H, $J = 9.0$ Hz, $\delta_A - \delta_B = 7.2$ Hz, C_6H_4), 7.35–8.25 (m, 8 H, NH and aromatic H), 8.50–8.92 (m, 2 H, 4- and 5-H); mass spectrum, *m/e* (relative intensity) 283 (M^+, 100), 282 (18), 267 (22), 165 (7). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.08; H, 6.18; N, 5.05.

Reaction of 18 with Hydrochloric Acid in Acetone. A solution of **18**[3c] (0.65 g, 2 mmol) in acetone (20 mL) containing hydrochloric acid (0.2 mL) was allowed to stand until gas evolution was complete (30 min). The resulting solution was evaporated under reduced pressure, and then the residue was extracted with ether. Removal of ether gave the solid, which was recrystallized from pentane to give 1-benzoyl-1-phenylcyclopropane (**20**): 0.43 g (97%); colorless microcrystals; mp 70–71 °C; IR 1670 cm^{-1} (CO); ^{1}H NMR δ 1.28 (m, AA′BB′, 4 H, CH_2CH_2), 6.80–7.75 (m, 10 H,

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[8] Burr, J. E., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 1717–1719.

[9] (a) Thiele, J.; Henle, H. *Justus Liebigs Ann. Chem.* **1906**, *347*, 290–314. (b) Kice, J. L. *J. Am. Chem. Soc.* **1958**, *80*, 348–352.

[10] (a) Lindsay, R. O. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, pp 710–711. (b) Ugi, I.; Perlinger, H.; Behringer, L. *Chem. Ber.* **1958**, *91*, 2330–2336.

[11] See paragraph at the end of the paper regarding supplementary material.

[12] Reddelien, G. *Chem. Ber.* **1910**, *43*, 2479.

[13] German Patent 650431, 1937; *Chem. Abstr.* **1938**, *32*, 952.[9]

aromatic H); mass spectrum, *m/e* (relative intensity) 222 (M^+, 69), 105 (100), 77 (51). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45: H, 6.35. Found: C, 86.44; H, 6.40.

After extraction, the residual solid, insoluble in ether, consisted of aniline hydrochloride, 0.25 g (98%).

Pyrolysis of 5. A solution of **5** (2 mmol) in xylene (10 mL) was refluxed until TLC showed the absence of **5** (∼3 h). The solvent was distilled off under reduced pressure, and the residue was recrystallized from benzene–hexane to give **9**. Results are shown in Table II.

Photolysis of 5. A solution of **5** (1 mmol) in benzene (50 mL) was irradiated at room temperature under nitrogen with a high-pressure mercury lamp through a Pyrex filter. After TLC showed the disappearance of **5**, the resulting solution was concentrated, and the residue was chromatographed to give **9** (a satisfactory isolation was not achieved) and a complex mixture of products. Results are shown in Table II.

Registry No. 3a, 4425-82-5; **3a** (polymer), 79918-16-4; **3b**, 1836-87-9; **4a**, 622-37-7; **4b**, 2101-86-2; **4c**, 2101-87-3; **4d**, 3296-05-7; **4e**, 1516-60-5; **5a**, 79918-17-5; **5b**, 79918-18-6; **5c**, 79918-19-7; **5d**, 79918-20-0; **9a**, 3920-79-4; **9b**, 79918-21-1; **9c**, 79918-22-2; **9d**, 79918-23-3; **9e**, 79918-24-4; **10a**, 79918-25-5; **10b**, 79918-26-6; **10c**, 79918-27-7; **10d**, 79918-28-8; **10e**, 79918-29-9; **11c**, 5455-02-7; **18**, 42540-65-8; **20**, 5685-39-2.

Supplementary Material Available: Characterization data of **5b–d**, **9c–e**, and **10b–e** (4 pages). Ordering information is given on any current masthead page.

Pyrolysis of the Tosylhydrazone Sodium Salts of Two Bicyclic Lactones

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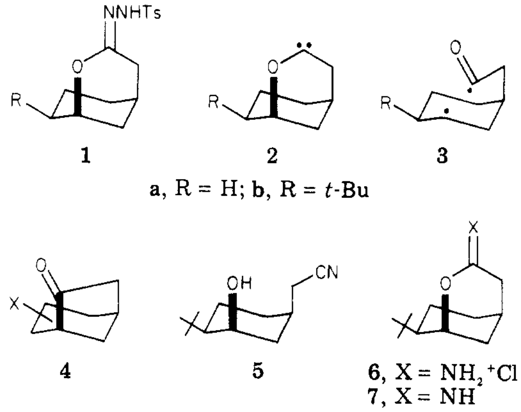
Lactone tosylhydrazone sodium salt **17a** was prepared from lactone **10** by way of thionolactone **14**. The *tert*-butyl homologue **17b** was available by way of hydroxy nitrile **5**. Pyrolysis of these salts led to enol ethers **18a,b** and the ring-contracted ketones **19a,b**. Together with earlier work, our results suggest that biradical **3** is probably an intermediate in conversion of alkoxycarbene **2** to ketone **4** and that the activation energy for this biradical coupling is ∼2–3 kcal/mol.

Earlier investigations in our laboratory demonstrated that pyrolysis of lactone tosylhydrazone sodium salts leads to cyclic alkoxycarbenes that generally undergo both a 1,2-shift of hydrogen and also carbon–oxygen bond scission to furnish alkyl acyl biradicals.[1,2] These biradicals collapse to cyclic ketones and, depending on the specific case, may also yield other products. In an investigation related to this earlier work, we have now prepared the bicyclic ketone tosylhydrazones **1a,b**, pyrolyzed the derived salts, and examined the products formed by way of the presumed alkoxycarbenes **2a,b** (Chart I). Our main purpose was to study the behavior of biradicals **3a,b** derived from the carbenes, to compare their behavior with each other, and to compare the behavior of these thermally generated singlet biradicals with that of closely related biradicals reached photochemically on irradiation of a number of substituted bicyclo[3.2.1]octan-6-ones (**4**).[3] Erratic distribution of pyrolytic products interfered with attainment of these goals, but the results do provide useful information on these topics and add to the rather meager information available on thermally generated alkoxycarbenes.[4] Preparative experiments are given first, followed by pyrolytic studies.

Chart I

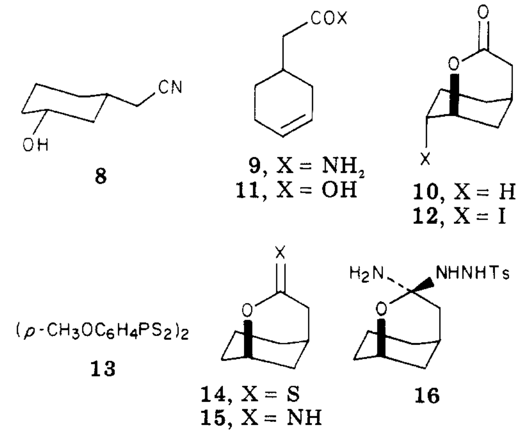


1 2 3

a, R = H; b, R = *t*-Bu

4 5 6, X = $NH_2{}^+Cl^-$ 7, X = NH

Chart II



8

9, X = NH_2 11, X = OH

10, X = H 12, X = I

$(p\text{-}CH_3OC_6H_4PS_2)_2$

13

14, X = S 15, X = NH

16

Preparative Experiments

The starting material for **1b** was the hydroxy nitrile **5** the preparation of which we have described elsewhere.[5] This substance underwent slow cyclization to the imidolactone hydrochloride **6** on exposure to dry hydrogen chloride in benzene.[6] Severe steric congestion about the

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[1] Foster, A. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 5777; **1973**, *95*, 608. Smith, A. B., III; Foster, A. M.; Agosta, W. C. *Ibid.* **1972**, *94*, 5100.

[2] Yates, P.; Loutfy, R. O. *Acc. Chem. Res.* **1975**, *8*, 209 and references cited therein.

[3] Agosta, W. C.; Wolff, S. *J. Am. Chem. Soc.* **1976**, *98*, 4182, 4316; **1977**, *99*, 3355.

[4] The statement that "alkoxycarbenes have proven extremely difficult to prepare by conventional synthetic methods" (Lucchese, R. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1978**, *100*, 298) is perhaps excessive, but it is certainly true that apart from photochemical work only a few studies of these species are on record.

[5] Ayral-Kaloustian, S.; Agosta, W. C. *J. Org. Chem.* **1981**, *46*, 4880.

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