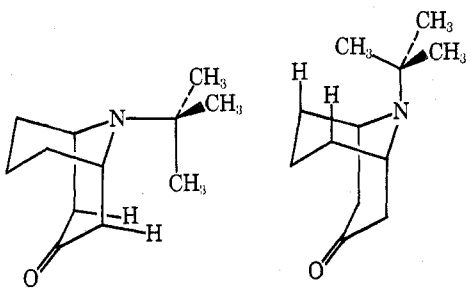
crements per methyl group are greater, especially with *tert*-butyl derivative **9**, at carbon 2(4) than at carbon 6(8). From



9

this we infer that, as the nitrogen atom undergoes pyramidal inversion, the *tert*-butyl group spends more time on the piperidone side of the molecule than on the piperidine side. This is probably due to flattening of the piperidone bridge in accommodating the sp^2-hybridized carbonyl carbon which diminishes somewhat the severity of the steric interactions. We have observed similar steric effects with the syn and anti epimers of 9-phenyl-9-phosphabicyclo-[3.3.1]nonan-3-one 9-oxide.[19]

Conclusion

With the results reported here, we have demonstrated the power of carbon-13 NMR spectroscopy in determining conformational preferences in bridged bicyclic substrates. Specifically, ^{13}C NMR spectroscopy can be utilized to ascertain simply the conformations and the configuration of 3-substituted and 9-substituted bicyclo[3.3.1]nonanes.

Experimental Section

The carbon-13 NMR spectra were measured at 25.15 MHz with a Jeol JNM PS-100 spectrometer interfaced with a Nova 1200 computer. The amines **1–9** were run in deuteriochloroform with tetramethylsilane as internal standard. The quaternary ammonium chlorides **11–13** were run in D_2O with the sodium salt of 3-trimethylsilylpropanesulfonic acid in D_2O as external reference. In all cases 10-mm tubes were employed and the sample concentrations were on the order of 0.5 *M*.

All of the amines utilized in this study were prepared according to literature procedures: **1**,[20] **2**,[21] **3**,[22] **4**,[23] **5**,[20] and **6–9**.[24] The quaternary ammonium chlorides **10–13** were prepared by the addition of excess methyl iodide to a solution of the corresponding amine in methylene chloride. The resulting precipitate was collected by filtration and then dissolved in hot water and passed through a 25 × 1 cm column packed with Amberlite IRA-401 ion exchange resin in the chloride form. Concentration of the eluent afforded the desired methochloride salts.

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Registry No.—**1**, 491-25-8; **2**, 2038-40-6; **3**, 6376-00-7; **4**, 56258-83-4; **5**, 56258-84-5; **6**, 552-70-5; **7**, 27092-59-7; **8**, 56258-85-6; **9**, 56258-86-7; **11**, 56258-87-8; **12**, 56258-88-9; **13**, 56258-89-0; methyl iodide, 74-88-4.

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Reaction of Azulene with Tetracyanoethylene Oxide

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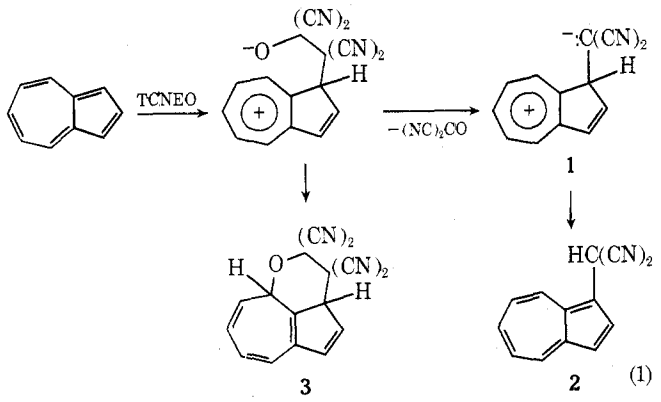
Azulene reacts with tetracyanoethylene oxide (TCNEO) to give 1-dicyanomethylazulene (**2**), 1-azuloyl cyanide (**4**), and 1-azulyltricyanoethylene (**6**) as the principal stable products. The major product was **4** (49%). The formation of **4** appears to involve carbon–carbon cleavage of the epoxide ring in TCNEO. A number of minor, unstable products were not characterized.

Tetracyanoethylene oxide (TCNEO) has been found to react readily with nucleophiles,[2,3,6] alkenes and alkynes,[2,4,5,7] aromatic rings,[2,4,5] Schiff bases,[6] and reducing agents.[5] The nucleophiles gave products derived from degradative scission of the epoxide ring, the alkenes gave stereospecific 1,3-dipolar-like addition, and the reducing agents abstracted oxygen and generated TCNE. With the aromatic compounds studied, which were all benzenoid and included benzene, naphthalene, anthracene, phenanthrene, furan, and thiophene, two distinct modes of reaction were

found: addition and oxidation. Oxidation was observed (accompanied by addition) for those systems having ionization potentials of 8.02 eV or less (anthracene, durene).

The nonbenzenoid azulene could act toward TCNEO as a nucleophile. This could lead to the electrophilic substitution product (**2**) via the established carbon–oxygen opening of the epoxide ring,[6] or the initial intermediate could undergo cycloaddition to form **3** (eq 1). Calculation of the ion-



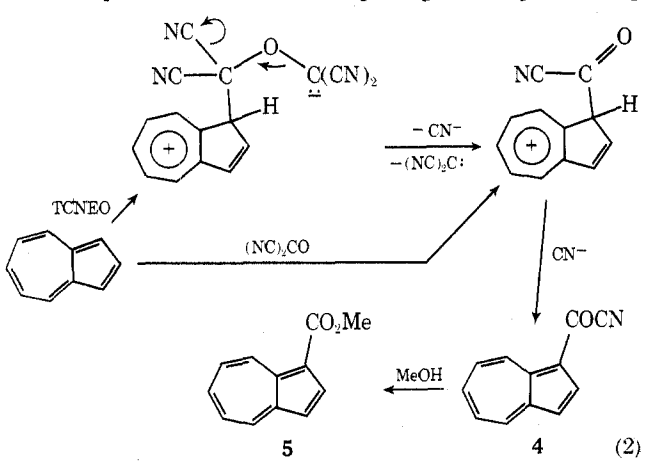
(1)

ization potential of azulene from the oxidation potential[8] gave a value of 6.867 eV, so oxidation would also be expected, probably with the generation of TCNE. To determine which of these reactions would occur, we have allowed azulene to react with TCNEO.

From the reaction in benzene at room temperature was obtained an almost black solid. Chromatography of this enabled the isolation of three stable products totaling 65.6% yield. In addition there were formed several unstable compounds which were not isolated in pure form and were not characterized.

The first product isolated was violet crystals which were identified to be 1-dicyanomethylazulene (**2**, 7.75%). The anticipated reactions leading to **2** thus possibly occurred, but to a perhaps surprisingly minor extent in view of striking reactivity of azulene to even weakly electrophilic reagents.[9]

The major product was 1-azuloyl cyanide (**4**), obtained as red-orange crystals (49%), a compound which had not been predicted. Two reasonable routes for the formation of **4** are shown (eq 2). The first involves opening of the epoxide ring



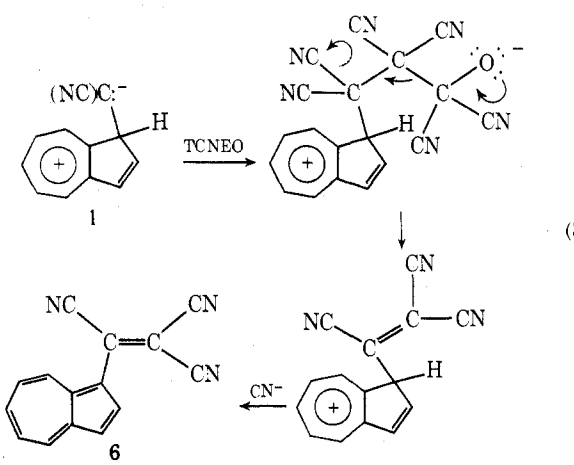
(2)

by carbon–carbon bond cleavage and thus possibly provides one of the few examples of this process.[10] The dicyanocarbene which would be generated could react with azulene to form **1**. This provides an alternative path to **2**. Evidence for this was provided by the reaction of azulene with bromomalononitrile, a precursor of dicyanocarbene, which gave **2** and also **6**. The finding of the latter, which in this case must arise from the reaction of azulene with tetracyanoethylene,[13] establishes the formation of dicyanocarbene in the reaction. Azulene apparently acts as the base needed. If pyridine was added prior to work-up, no **6** was isolated, indicating a reaction of this product with the base. Curiously, in the presence of triethylamine the products were 1,3-dibromoazulene and **6**. This result calls for an electrophilic bromine compound and the bromotriethylammonium ion is suggested.

The second route is direct electrophilic substitution by reaction with carbonyl cyanide, and its simplicity makes it attractive. The plausibility of this was shown by a test reaction which afforded **4** in 80% yield. This route requires, however, a source of carbonyl cyanide corresponding to the amount of **4** formed. The reaction yielding **1** would provide only ca. 8% and other sources for the additional 41% were not evident. Therefore, the indirect path is considered to be the more probable.

Additional characterization of **4** was provided by its reaction with methanol to form the known methyl 1-azuloate (**5**)[11] in essentially quantitative yield, and its preparation from azulene by reaction with phosgene and then cuprous cyanide. Compound **4** was also formed (87%) during the chromatography of **2** on Florisil[12] in the presence of wet ether. As the material moved down the column, the green color from **2** gradually changed to orange. This reaction involves an oxidation, yet the $MgO{\cdot}SiO_2$ with ca. 0.5% Na_2SO_4 composition of the adsorbent would not seem to provide this. The nature of the oxidizing agent was not determined.

A third stable product was 1-azulyltricyanoethylene (**6**, 8.8%), which has been shown to be formed from the reaction of azulene with TCNE[13] or chlorotricyanoethylene.[14] The isolation of **6** and the fact that a number of unstable products were observed in other chromatographic fractions is consistent with TCNE being formed from a reaction of TCNEO with azulene wherein the latter is oxidized. An alternative route to **5** would require that the second intermediate (**1**) leading to **2** exist long enough to react with a second molecule of TCNEO as shown (eq 3). This is considered to be less likely.



(3)

Experimental Section

Melting points are corrected. Uv and visible spectra were recorded on a Cary Model 14 recording spectrophotometer. Ir spectra were recorded with a Perkin-Elmer Model 21 instrument. NMR spectra were taken on a Varian Model A-60 or T-60 with Me_4Si as internal reference. Analyses were performed by Mr. Dave Harsch at the University of Idaho or by Chemalytics, Inc., Tempe, Ariz. All solvents were reagent grade or purified prior to use. Silica gel for chromatography was Davison or, for final purification, Mallinckrodt SiliAR CC-7.

Reaction of Azulene with Tetracyanoethylene Oxide. To a stirred solution of 522.3 mg (4.08 mmol) of azulene[15] in 20 ml of dry benzene at room temperature was added dropwise over 1 hr a

solution of 579.9 mg (4.03 mmol) of freshly sublimed, pure (mp 179–179.5°) TCNEO[16] in 130 ml of benzene and the mixture was stirred for an additional 1 hr. Removal of the solvent (reduced pressure) left an almost black solid which was dissolved in 30 ml of benzene and chromatographed on a silica (70 g) column with benzene (1 l.), THF (1 l.), and MeOH (1 l.) as the eluents in that order. The last appeared to contain only unstable products which were not characterized.

The residue (570.1 mg) from the benzene eluate contained three products (TLC on silica gel, R_f 0.13, 0.18, and 0.22 with benzene) and the benzene eluate (ca. 0.5 l.) from the chromatography of this on silica gel (40 g) was collected first in ca. 10-ml fractions and these were then combined according to color into seven fractions. From fraction 1 was obtained 0.5 mg of unchanged azulene. Chromatography of an ether solution of the residue (104.2 mg of brown crystals) from fraction 2 on silica gel (60 g) afforded 58.6 mg (7.54%) of 1-dicyanomethylazulene (**2**) as violet crystals which formed plates when crystallized from *n*-hexane–benzene: mp 140.3–141.3°; uv ($HCCl_3$) 223 nm (log ϵ 4.72), 241 (sh, 4.24), 268 (sh, 4.48), 274 (sh, 4.66), 278 (4.78), 283 (4.74), 288 (4.77), 339 (3.74), and 355 (3.60); visible ($HCCl_3$) 473 nm (sh, ϵ 172), 512 (366), 560 (522), 600 (453), and 656 (sh, 177); ir ($HCCl_3$), 2265 (CN), 2915 and 2880 cm^{-1} (CH); NMR ($DCCl_3$) δ 5.63 (s, 1, –CH<), 7.44 (d, 1, J = 4.0 Hz, H-3), 7.30–7.98 (AB_2, 3, H-5, H-6, H-7), 8.07 (d, 1, J = 4.0 Hz, H-2), 8.42 (d of d, 1, J = 9.8 and 1.2 Hz, H-4), 8.52 (d, 1, J = 9.8 and 1.2 Hz, H-8).

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.57. Found: C, 81.35; H, 4.20; N, 14.20.

Rechromatography of fraction 3 (12.3 mg of reddish brown crystals) gave an additional 2.2 mg of **2** for a total yield of 60.8 mg (7.83%).

Rechromatography of the residue (313.2 mg of orange crystals) from fraction 4 on 20 g of silica gel separated 304.4 mg (40.4%) of 1-azuloyl cyanide (oxo-1-azulylethanenitrile) as reddish orange crystals, mp 140.2–140.5° after recrystallization from *n*-hexane–benzene: uv ($HCCl_3$) 222 nm (log ϵ 4.53), 2.77 (4.08), 323 (4.36), 403 (4.16), and 419 (4.17); visible ($HCCl_3$) 500 (ϵ 1021), 541 (sh, 685) and 586 (sh, 180); ir ($HCCl_3$) 1635 (CO) and 2330 cm^{-1}, (CN); NMR ($DCCl_3$) δ 7.38 (d, 1, J = 4.5 Hz, H-3), 7.60–8.30 (ABC, 3, H-5, H-6, H-7), 8.46 (d, 1, J = 4.5 Hz, H-2), 8.65 (d of d, 1, J = 9.8 and 2.0, H-4), 9.75 (d of d, 1, J = 9.5 and 2.0 Hz, H-8); MS (70 eV) *m/e* (rel intensity) 181 (59.4) (P^+), 155 (100) (P – CN), and 127 (36.9) (P – CNCO).

Anal. Calcd for $C_{12}H_7NO$: C, 79.55; H, 3.89; N, 7.75. Found: C, 79.55; H, 3.92; N, 7.75.

From the rechromatography of fractions 2 and 3 (see above), fraction 5 (9.1 mg of red crystals), and fraction 6 (70.7 mg of dark brown solid) was obtained 25.5 mg of **4** for a combined yield of 329.9 mg (45.1%). The residue (492.5 mg) from the original THF eluate was chromatographed on 75 g of silica gel with ca. 0.5 l. of THF–5% MeOH as the eluent as described above for the benzene eluate fraction except that the small fractions were combined into nine fractions according to color. The last seven were found to contain small quantities of unstable products which were not characterized. Rechromatography twice more of the combined residues from fraction 1 (19 mg of reddish brown crystals) and fraction 2 (224.9 mg of brown oil), and of fraction 7 (22.6 mg of brown solid) from the benzene eluate fraction, with benzene as the eluent gave an additional 32 mg of **4** for a total yield of 361.9 mg (49.44%).

From the above chromatograph of fraction 4 was obtained 1.2 mg of red-brown crystals which was combined with the major component of fraction 6. Rechromatography of the combined material (15 g of silica gel, benzene) afforded 65.2 mg (7.06%) of 1-azulyltricyanoethylene (**6**) as reddish brown needles: mp 202.8–203.2° (lit.[13,14] 201–202°) after recrystallization from benzene; uv ($HCCl_3$) 234 nm (log ϵ 4.13), 256 (4.12), 302 (4.06), 366 (3.80), and 384 (sh, 3.72); visible ($HCCl_3$) 495 (4.43), 530 (sh, 4.23), and 567 (sh, 3.66); ir ($HCCl_3$) 1585, 1605 (C=C), and 2230 cm^{-1} (CN); NMR (Me_2SO-d_6) δ 7.78 (d, 1, J = 4.8 Hz, H-3), 7.88–8.48 (AB_2, 3, H-5, H-6, H-7), 8.57 (d, 1, J = 4.8 Hz, H-2), 8.95 (d of d, 1, J = 9.5 and 1.5 Hz, H-4), and 9.27 (d of d, 1, J = 9.5 and 1.5 Hz, H-8).

From the rechromatography of fractions 1 and 2 of the original THF eluate (see above) was obtained an additional 16 mg to make the total yield 82.3 mg (8.9%) of **6**.

1-Azuloyl Cyanide (4). A. From 1-Azulyldicyanoethylene (2). A solution of 2.9 mg (0.015 mmol) of **2** in 2 ml of ether was chromatographed on 10 g of Florisil.[12] The violet color changed to green as the material was adsorbed, and then gradually to orange as the chromatogram developed. Ether saturated with water was the eluent and the time on the column was 2 hr. The residue (2.8 mg) from the orange eluate was rechromatographed in the same manner to give 2.3 mg (87%) of **4** identified by comparison of its ir spectrum and TLC behavior with those of an authentic sample.

B. From Azulene, Phosgene, and CuCN. A saturated solution of phosgene (ca. 2 mmol) in 0.4 ml of dry benzene was added slowly (syringe) to a stirred, ice-cooled solution of 12.8 mg (0.1 mmol) of azulene in 2 ml of dry benzene. The mixture was allowed to come to room temperature as stirring was continued (3 hr). Two further additions [ca. 3 mmol (0.6 ml) and 5 mmol (1 ml)] of the phosgene solution were made at hourly intervals with stirring continued for 1 hr after the last addition. The dark red, semisolid residue (presumed to contain 1-azuloyl chloride) was stirred with 13.5 mg (0.15 mmol) of dried (110°) CuCN and 8 ml of dry pyridine for 4 days. Evaporation of the pyridine (vacuum pump) left a dark red solid which was chromatographed on silica gel (7 g). Elution with benzene afforded 0.1 mg of unchanged azulene and 2.7 mg (15%) of **4** as orange-red crystals identical (ir and TLC) with the material from A. Elution with THF removed 12.4 mg of dark violet crystals (three components by TLC) which were not investigated further.

C. From Azulene and Carbonyl Cyanide. To an ice-cooled solution of 12.8 mg (0.1 mmol) of azulene in 2 ml of dry benzene was added dropwise (5 min) with stirring 8 mg (0.1 mmol) of carbonyl cyanide.[3] The cold mixture was stirred for an additional 25 min and then the solvent was slowly removed under reduced pressure at 0°. Chromatography of the residue on 5 g of SiO_2 with benzene as the eluent gave 2 mg (16%) of unchanged azulene and then 14.5 mg (80.1%) of **4** as orange crystals identical (TLC and ir) with an authentic sample.

Methyl 1-Azuloate (5) from 1-Azuloyl Cyanide (4). A solution of 21.9 mg (0.121 mmol) of **4** in 4 ml of absolute MeOH was shaken occasionally for 30 min, during which time the color changed from orange to red to purple. The solution was then refluxed for 10 min. After removal of the solvent (reduced pressure), the residue was chromatographed on silica gel (15 g, benzene eluent) and 22.3 mg (99.2%) of **5** was obtained as a purple liquid identical (TLC, ir) with an authentic sample.[9b]

Reaction of Azulene with Bromomalononitrile. A. A solution of 18 mg (0.12 mmol) of bromomalononitrile[17] in 1 ml of dry acetonitrile was added dropwise to 12.8 mg (0.1 mmol) of azulene dissolved in 2 ml of acetonitrile. After 16 hr, the solvent was carefully evaporated (reduced pressure) and a solution of the residue in 3 ml of benzene was chromatographed on 7 g of SiO_2. Following a small yellow oil fraction which was not characterized, there was obtained 2.8 mg (15%) of **2** as violet crystals identical (TLC, uv, ir) with an authentic sample, and 4.5 mg (20%) of **6** as red crystals identical (TLC, ir) with the product previously obtained.

B. To an ice-cooled solution of 12.8 mg (0.1 mmol) of azulene and 12 mg (0.12 mmol) of triethylamine in 2 ml of dry acetonitrile under N_2 was added dropwise with stirring a solution of 18 mg (0.12 mmol) of bromomalononitrile in 1 ml of acetonitrile. The mixture was stirred for 5 min, the solvent was carefully removed under reduced pressure, and the residue was chromatographed (benzene) on 7 g of SiO_2. The first blue fraction yielded 7.5 mg (26%) of 1,3-dibromoazulene, and the red eluate yielded 0.3 mg (1%) of **6** identical (TLC, ir) with authentic samples of each.

Registry No.—**2**, 56454-36-5; **4**, 56454-37-6; **6**, 56454-38-7; azulene, 275-51-4; tetracyanoethylene oxide, 3189-43-3; bromomalononitrile, 1885-22-9.

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