acetylene.[5] It appears that hydroboration of acetylenes is not a cleanly predictable reaction but leads to a mixture of products

Experimental

All melting points are uncorrected. Infrared spectra were run in potassium bromide on a Beckman I R 5 instrument.

Reaction of Diphenylacetylene (I) with Diborane.—Diphenylacetylene (I), m.p. 60–61°, was prepared from stilbene *via* the dibromide.[6] Its infrared spectrum, by comparison with spectra of mixtures of diphenylacetylene and stilbene, indicated the presence of less than 2% of stilbene if any. Into a solution of 1.0 g. of diphenylacetylene (I) in dry tetrahydrofuran at 0° was passed diborane, generated from 3 g. of sodium borohydride and excess boron trifluoride etherate in diglyme. The solution was kept at 4° for 14 hr. Excess diborane was destroyed by addition of ice and the mixture was stirred with 25 ml. of 3 *N* sodium hydroxide and 15 ml. of 25% hydrogen peroxide for 40 min. The mixture was extracted with ether. The organic layer was washed with ferrous sulfate solution, then five times with water, dried, and evaporated. The residue (1.05 g.) was taken up in benzene and chromatographed over 30 g. of Merck aluminum oxide. The eluted fractions were evaporated and the residues identified by infrared, melting point, and mixed melting point comparison with authentic samples. The following results were obtained: Fraction 1 (35 mg.) melted at 125°. Upon crystallization from aqueous alcohol and then from petroleum ether (b.p. 40–60°) it gave material melting at 124–126°; mixed with *trans*-stilbene, m.p. 127°, it melted at 124–126°.

Fractions 2–4 (34 mg. of an oil that slowly crystallized) were identified by infrared and through its 2,4-dinitrophenylhydrazone, m.p. 203–205°, as desoxybenzoin.

Fraction 5 (453 mg.) melted at 46–56° and upon crystallization from petroleum ether (b.p. 60–90°) at 59–62°. Mixed melting point and infrared comparison with authentic material, m.p. 65°, prepared by hydroboration of *trans*-stilbene, identified it as 1,2-diphenylethanol (VI).

Fraction 6 (78 mg.) was a mixture difficult to separate.

Fractions 7–9 (372 mg.) were essentially *d,l*-dihydrobenzoin (V). Crystallization from water followed by drying and recrystallization from petroleum ether (b.p. 60–90°) gave material, m.p. 120–120.5°, identical in all respects with authentic *d,l*-dihydrobenzoin, prepared from benzil.

Fractions 10–11 (17 mg.) were likewise slightly impure *d,l*-dihydrobenzoin.

Acknowledgment.—We gratefully acknowledge financial support (Grant CY-4474) by the National Institutes of Health.

(5) T. J. Logan and T. J. Flautt, *J. Am. Chem. Soc.*, **82**, 3446 (1960).

(6) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1957, p. 181.

Some Studies on Tropenylazulenes[1,2]

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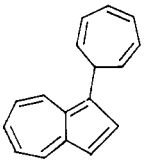
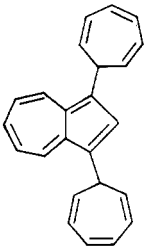
The recent publication of the reaction of azulene with tropenium perchlorate and of an attempt to obtain the interesting (1-azulyl)tropenium ion[5] prompt us to report the results of similar, independent studies. Our objectives were, first, the preparation of tropenylazulenes[6] and, second, the removal of a hyride ion to form a (1-azulyl)tropenium ion structure.

Treatment of azulene with tropenium fluoroborate afforded two crystalline products, 1-tropenylazulene (I) and 1,3-dinitropenylazulene (II). The latter was the principal product even when an excess of azulene was used.[7] With a 50% excess of azulene, for example, 19% of I and 51% of II were obtained, and if one equivalent of pyridine was present the yield of II was 62%.

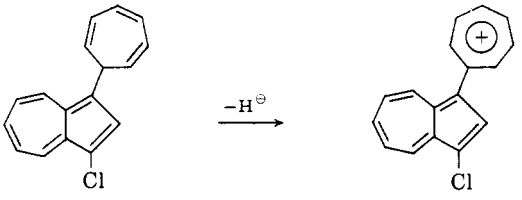


I



II

As the formation of a (1-azulyl)tropenium ion would involve reaction with a positive species, a 1-tropenylazulene having a simple, inert substituent in the nucleophilic 3-position was desired and 1-tropenyl-3-chloroazulene (III) was chosen. The reaction of 1-chloroazulene with tropenium fluoroborate gave a blue oil which exhibited an absorption maximum in the visible spectrum corresponding to that expected for III,[8] but was unaccountably difficult to purify and gave only fair analytical values. The n.m.r. spectrum was consistent with the assigned structure. There were three sets of multiplets centered at *ca.* 3.3, 3.8, and 4.57 p.p.m., each of relative intensity two, for the three types of vinyl protons, and a triplet at 6.67 p.p.m. of intensity one for the saturated hydrogen. The remainder of the spectrum corresponded to that of a 1,3-disubstituted azulene.[9] The further fact that this same substance was formed by the reaction of I with N-chlorosuccinimide established its identity sufficiently to permit its use in the hydride exchange experiments.



III IV

The addition of a slight excess of triphenylmethyl fluoroborate to a solution of III in dry acetonitrile caused a rapid color change from blue to green. From the reaction mixture were isolated a small amount of a colorless solid identified as tropenium fluoroborate by its ultraviolet spectrum, a low yield of triphenylmeth-

(1) From the Ph.D. thesis of Lanny L. Replogle, University of Washington, July, 1960.

(2) Supported in part by a grant (G 7397) from the National Science Foundation.

(3) National Science Foundation Senior Postdoctoral Fellow, 1960–1961.

(4) National Science Foundation Coöperative Fellow, 1959–1960. Present address: Department of Chemistry, San Jose State College, San Jose, Calif.

(5) K. Hafner, A. Stephan, and C. Bernhard, *Ann.*, **650**, 42 (1961).

(6) Tropenyl will be used as the name for the 7-cycloheptatrienyl group.

(7) K. Hafner, *et al.* (ref. 5), reported II to be the sole product of their analogous reaction.

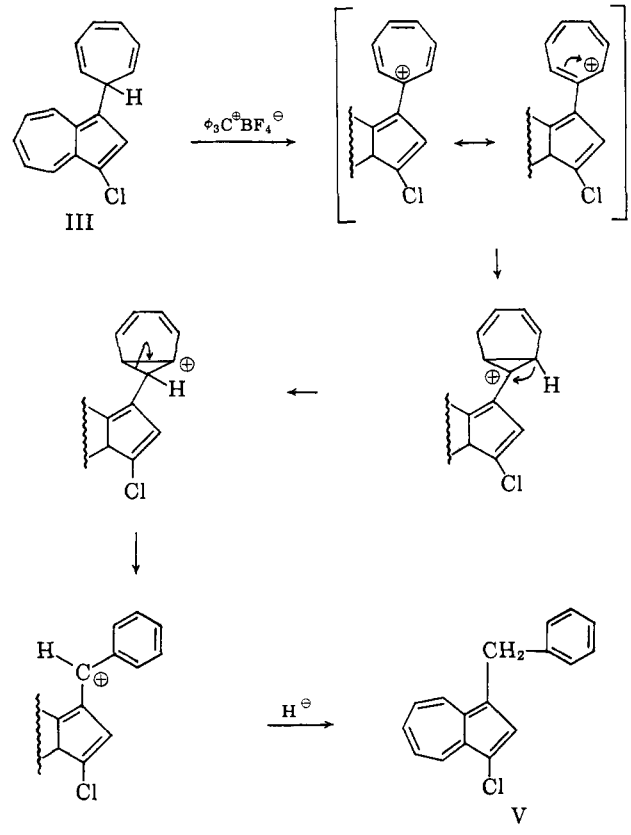
(8) λ_{max} (obsd.) 628 mμ, λ_{max} (calcd.) 630 mμ based on $\Delta\lambda_{max}$ for the chloro group as +30 mμ [*cf.* E. J. Cowles, *J. Am. Chem. Soc.*, **79**, 1093 (1957)], and $\Delta\lambda_{max}$ for the tropenyl group as +20 mμ (see Experimental).

(9) A. G. Anderson and L. L. Replogle, unpublished results.

ane, some 1-triphenylmethyl-3-chloroazulene, and a brown, gummy material. The formation of triphenylmethane showed that some hydride exchange had occurred. The identity of the 1-triphenylmethyl-3-chloroazulene was established by the formation of an identical product from the triphenylmethylation of 1-chloroazulene. These findings are most plausibly explained in terms of the formation of an azulyltropenium ion (IV) and subsequent electrophilic displacement of the tropenium moiety by the triphenylcarbonium ion. The latter step finds analogy in the elimination of the tropenium ion from β-tropenylalkyl halides[10] and identical behavior was observed by Hafner, *et al.*[5] The facility with which groups which can form stable positive ions undergo this type of displacement has been noted with a number of 1,3-disubstituted azulenes.[11]

Further evidence for the existence of IV was sought in the brown, gummy material. The infrared spectrum of this had a large, broad peak in the 9–10-μ region which is characteristic of the fluoroborate ion.[12] The dark green solution formed with methylene chloride[5] showed a strong peak at 485 mμ and azulene-like absorption in the ultraviolet. Reid, *et al.*,[13] have found strong absorption in the region 450–500 mμ for most 1-substituted azulenium salts. As was the case in the study by Hafner and co-workers,[5] all efforts to isolate a pure substance were unsuccessful. The addition of a hydride ion to IV would be expected to occur on the tropenyl ring to regenerate III and/or tautomeric isomers. As tropenium salts are reduced by sodium borohydride in good yield,[14] the brown, gummy product from one run was treated with this reagent. There were obtained triphenylmethane and two oils which appeared to be isomeric with III. One of these and an oil obtained from the mixture prior to the addition of sodium borohydride, both green in color, showed essentially identical absorptions in the ultraviolet and visible regions which were also very similar to those of III, but differed slightly in their infrared spectra from each other and from III, and are postulated to be tautomeric isomers of III. To see if such a product might have been formed *via* III by the presence of excess sodium borohydride, III was treated with this reagent under the same reaction conditions. Only unchanged III was recovered. The other oil, blue-green in color, likewise had a visible spectrum almost identical to that of III but differed in absorption in both the ultraviolet and infrared regions. The n.m.r. spectrum of this material showed a split peak (τ = 2.87 and 2.90) of relative intensity very close to five[15] and an unsplit saturated hydrogen peak at τ = 5.7 of intensity two, but no indication of vinyl hydrogens. A structure consistent with these data is 1-benzyl-3-chloroazulene (V) and this suggestion was confirmed by comparison of the ultraviolet, visible, infrared, and n.m.r. spectra of material prepared by the chlorination of 1-benzylazulene with those of the reduction product.

The formation of V can be explained as shown. In view of the fact that III was shown to be unaffected by the sodium borohydride, and therefore a base-catalyzed rearrangement such as occurs with certain tropolones[16] is excluded, it is difficult to envision any reasonable alternative route. If V did arise from IV this represents the first example of the rearrangement of a tropenium ion to a benzyl cation.[17] In the present system



the benzylazulyl cation could well be the more stable structure as it would appear to have appreciably less steric hindrance to complete conjugation than the azulyltropenium ion.

The failure to isolate a pure azulyltropenium salt was not unexpected in that Kirby and Reid[18] found that only aromatic aldehydes with electron-releasing groups gave isolable salts upon condensation with azulene, and even these decomposed upon attempted recrystallization.

(10) K. Conrow, *J. Am. Chem. Soc.*, **79**, 1093 (1957).

(11) A. G. Anderson and R. N. MacDonald, *ibid.*, **81**, 5669 (1959); A. G. Anderson, R. Scotoni, E. J. Cowles, and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957); A. G. Anderson, J. A. Nelson, and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953).

(12) C. L. Coté and W. W. Thompson, *Proc. Roy. Soc.* (London), [A], **210**, 217 (1951); B. P. Susz and J.-J. Wuhrmann, *Helv. Chim. Acta*, **40**, 722 (1957).

(13) D. H. Reid, W. H. Stafford, W. L. Stafford, G. MacLennan, and A. Voight, *J. Chem. Soc.*, 1110 (1958).

(14) H. J. Dauben and L. McDonough, private communication.

(15) The occurrence of the bands from the 5- and 7-hydrogens in the same region precluded an exact measurement of the intensity. The split maximum was attributed to the presence of a small amount of 1-triphenylmethyl-3-chloroazulene as the triphenylmethyl group was shown to give two aromatic hydrogen peaks at τ = 2.88 and 2.93, and the sample of pure 1-benzyl-3-chloroazulene gave a single peak at τ = 2.89.

(16) *Cf.* T. Nozoe, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, ed., Interscience Publishers, Inc., New York, N. Y., 1959, chap. 7.

(17) Subsequently H. J. Dauben and D. Bertelli (private communication) obtained 7-benzylcycloheptatriene from the reaction of ditropenyl with triphenylcarbonium hexachloroantimonate. In this case the intermediate tropenyltropenium salt could be isolated and solutions of this were observed to undergo the rearrangement. The conversion of tropenium ion to benzaldehyde by the action of bromine probably proceeds through a cycloheptatriene intermediate.[13]

(18) E. C. Kirby and D. H. Reid, *J. Chem. Soc.*, 494 (1960).

Experimental[19]

1-Tropenylazulene (I) and 1,3-Ditropenylazulene (II).—To a solution of 192 mg. (1.5 mmoles) of azulene and 0.08 ml. (1 mmole) of pyridine in 20 ml. of reagent grade anhydrous methanol was added 178 mg. (1 mmole) of tropenium fluoroborate, and the mixture was allowed to stand at room temperature for 2 hr. and 50 min. It was then warmed on a steam bath for 10 min., poured into water, and extracted with ether. The residue from the ether extract was carefully chromatographed over basic alumina. Continued washing with petroleum ether developed a blue-purple band and two blue bands and from the first, which was eluted with this solvent, was obtained 113 mg. of azulene. The remaining two bands were eluted with a 50:1 petroleum ether–methylene chloride mixture. Rechromatography of the residue from the first blue fraction afforded 42 mg. (19%) of crystalline 1-tropenylazulene, m.p. 55–58°. The analytical sample prepared by sublimation under reduced pressure consisted of blue needles, m.p. 59–60.5°. A cyclohexane solution showed λ_{max} in mμ (ϵ) in the ultraviolet at 241 (19,000), 279 (48,000), 331 (3200), 337 (3400), 345 (5200), 362 (3000) and shoulders at 283 (44,000), 323 (2300), 334 (3300), and 359 (2500), and in the visible at 601 (320), 625 (280), 656 (280), and 724 (110) with shoulders at 561 (230), 580 (270), and 687 (140).

Anal. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.12; H, 6.51.

Removal of the solvent from the second blue fraction gave 96 mg. (62%) of 1,3-ditropenylazulene as dark blue blades, m.p. 133–135°. A sample recrystallized from methylcyclohexane melted at 135–136°.[5] A cyclohexane solution exhibited λ_{max} in mμ (ϵ) in the ultraviolet at 243 (29,000), 282 (48,000), 347 (7000) and 364 (5500), and in the visible at 619 (370), 674 (320), and 753 (120) with shoulders at 574 (260) and 645 (320).[5] The n.m.r. spectrum showed resonance peaks centered at 6.65 p.p.m. (saturated hydrogens), 4.45, 3.77, and 3.26 p.p.m. (three types of vinyl hydrogens), and for the azulene ring hydrogens at *ca.* 3.11 p.p.m. (5- and 7-positions), 2.57 p.p.m. (6-position), 1.88 p.p.m. (4- and 8-positions), and 1.87 p.p.m. (2-position) of the expected intensity and multiplicity.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.73; H, 6.48.

1-Tropenyl-3-chloroazulene (III). A. From 1-Chloroazulene.—To 51.5 mg. (0.317 mmole) of 1-chloroazulene dissolved in 10 ml. of ethanol was added 53 mg. (0.298 mmole) of tropenium fluoroborate. The mixture was allowed to stand at room temperature for 2 hr. and 15 min. and was then poured into a dilute sodium bicarbonate solution. The whole was extracted with methylene chloride, and the solvent was removed from the organic extracts. The residual blue oil was chromatographed over activated basic alumina. Petroleum ether developed two blue bands and the first, which was small, was eluted with this solvent. A 25:1 petroleum ether–methylene chloride mixture eluted the main band and removal of the solvent from this gave 63 mg. (83%) of 1-chloro-3-tropenylazulene as a blue oil. A cyclohexane solution showed peaks in mμ (ϵ) in the ultraviolet at 242 (24,000), 286 (49,000), 352 (5700), 366 (4700), and 371 (5100) with shoulders at 328 (2500) and 341 (3800), and in the visible at 628 (420), 687 (350), and 765 (130) with shoulders at 583 (300), 606 (360), 656 (360), and 730 (160). The infrared spectrum was recorded. The n.m.r. spectrum showed resonance peaks centered at 6.77 p.p.m. (saturated hydrogen), 4.57, 3.8, and 3.27 p.p.m. (three types of vinyl hydrogens), and for the azulene ring hydrogens at *ca.* 3.0 p.p.m. (5- and 7-positions), 2.54 p.p.m. (6-position), 2.10 p.p.m. (2-position), and 1.98 and 1.75 p.p.m. for the 4- and 8- (or 8- and 4-) positions of the expected intensity and multiplicity.

Anal. Calcd. for $C_{17}H_{13}Cl$: C, 80.79; H, 5.18. Found: C, 81.28; H, 5.31.

B. From 1-Tropenylazulene.—A mixture of 19 mg. (0.087 mmole) of 1-tropenylazulene, 13 mg. (0.097 mmole) of N-chlorosuccinimide, and 5 ml. of dimethylformamide was allowed to stand at room temperature for 12 hr. and was then poured into water. The whole was extracted with ether and the separated ethereal solution washed throughly with water. Removal of the solvent from the organic layer left a blue oil which was chromatographed over basic alumina. Petroleum ether developed two blue bands; the first of these was removed with 25:1 petroleum ether–methylene chloride and the second with a 10:1 mixture of the same solvents. The second fraction yielded 11 mg. (50%) of a blue oil which was identical (ultraviolet, visible, and infrared spectra) to the material obtained in method A.

1-Triphenylmethyl-3-chloroazulene.—To 119 mg. (0.735 mmole) of 1-chloroazulene in 20 ml. of acetonitrile was added 240 mg. (0.728 mmole) of triphenylmethyl fluoroborate. The mixture was allowed to stand at room temperature for about 30 min., was then poured into water and the whole was extracted with methylene chloride. The organic extracts were washed with water, the solvent then removed, and the blue crystalline residue was chromatographed over basic alumina. Petroleum ether developed a small and a large blue band. The former was eluted with 10:1 petroleum ether–methylene chloride and from this fraction were obtained 13 mg. of 1,3-dichloroazulene.[20] Continued elution removed the larger band and the residue from this eluate amounted to 223 mg. (76%) of 1-triphenylmethyl-3-chloroazulene, m.p. 199–203°, after recrystallization from ligroin. The analytical sample recrystallized from methanol as large blue plates, m.p. 204–206°. A cyclohexane solution exhibited λ_{max} in mμ (ϵ) in the ultraviolet at 243 (33,000), 292 (62,000), 349 (3900), 359 (5700), 368 (3800), and 377 (6900) with shoulders at 287 (56,000), 302 (52,000), 334 (2300), and 344 (3400), and in the visible at 630 (440), 687 (360), and 767 (120) with shoulders at 585 (120) and 662 (360).

Anal. Calcd. for $C_{29}H_{21}Cl$: C, 86.01; H, 5.23. Found: C, 86.35; H, 5.31.

Reaction of 1-Tropenyl-3-chloroazulene with Triphenylmethyl Fluoroborate.—About 20 ml. of dry acetonitrile was distilled from a flask containing phosphorus pentoxide into a 100-ml. round-bottomed flask which contained 78 mg. (0.308 mmole) of 1-tropenyl-3-chloroazulene. Triphenylmethyl fluoroborate (103 mg., 0.312 mmole) was then added quickly, the flask was stoppered, and the mixture, which quickly turned green, was allowed to stand for 20 hr. Removal of the solvent with a rotary evaporator left a dark brown solid. This was triturated with two 100-ml. portions of dry petroleum ether. The extracts, which were blue, were set aside. The gummy residue was treated with about 15 ml. of methylene chloride and the dark green solution which resulted decanted from some colorless crystals. A solution of the latter in sulfuric acid gave an ultraviolet spectrum identical with that with an authentic sample of tropenium fluoroborate. The green methylene chloride solution exhibited λ_{max} in mμ (D_{max}) in the ultraviolet at 287 (2.90), 296 (2.7), 324 (0.8), 373 (0.7), and 392 (0.7), and in the visible at 485 (1.2), 620 (0.3), and 675 (0.4). Removal of the solvent and trituration of the residue with two 50-ml. portions of dry ether gave a gummy brown residue and a blue ether solution. The latter was combined with the petroleum ether extracts of the same color. Chromatography of the residue from this solution over basic alumina with prolonged elution with petroleum ether separated 28 mg. (37%) of triphenylmethane, m.p. 84–89°. A sample crystallized from ethanol melted at 90–92° alone and at 91–93° when mixed with an authentic sample. The ultraviolet spectra of the product and sample were identical. The first of two blue bands which had developed was eluted with a 25:1 petroleum ether–methylene chloride mixture, and the second (smaller) band with a 1:1 mixture of the same solvents. The first fraction contained 31 mg. (25%) of 1-triphenylmethyl-3-chloroazulene identical (m.p., m.m.p., ultraviolet and visible spectra) with an authentic sample.[21] The solid material from the second fraction (*ca.* 7 mg.) contained triphenylcarbinol but was not investigated further. The gummy brown residue [presumed to be mostly [1-(3-chloroazulyl)]tropenium fluoroborate (IV)] showed a large, broad peak at 9–10 μ[12] and slowly turned purplish blue on standing. The shaking of a green methylene chloride solution (λ_{max} at 485 mμ[13]) of it with water caused the color of both phases to become blue

(19) Melting points are uncorrected and were taken on a Fisher–John apparatus. Ultraviolet and visible absorption spectra were recorded with a Model 11S or 14 Cary recording spectrophotometer. Infrared spectra were obtained with a Perkin–Elmer Model 21 recording spectrophotometer. The n.m.r. spectra were recorded by Mr. B. J. Nist with a 60-Mc. Varian Associates high resolution spectrometer with carbon tetrachloride as the solvent and with tetramethylsilane or hexamethyldisilane as an internal standard. Elementary analyses were performed by Drs. G. Weiler and F. B. Strauss, Microanalytical Laboratory, Oxford, England, and by Dr. Alfred Bernhardt, Microanalytical Laboratory, Max-Planck Institute, Mülheim (Ruhr), Germany.

(20) This materially was presumably present as an impurity in the 1-chloroazulene used.

(21) In qualitative experiments tropenium fluoroborate was also obtained from reactions of III with excess triphenylmethyl fluoroborate in methylene chloride or chloroform, and 1-triphenylmethyl-3-chloroazulene was isolated from a reaction of III and *ca.* an equivalent amount of triphenylmethyl fluoroborate.

and then all of the colored material went into the organic layer; the blue solid recovered could not be crystallized. Efforts to obtain material of analytical purity corresponding to IV were unsuccessful.

1-Benzyl-3-chloroazulene (V).—To a solution of 35.5 mg. (0.163 mmole) of 1-benzylazulene in 10 ml. of dimethylformamide was added 22 mg. (0.165 mmole) of N-chlorosuccinimide. The reaction mixture slowly turned green and after a few hours it was allowed to stand in a refrigerator (at *ca.* 10°) overnight. The mixture was poured into water, the whole extracted with ether, and the green ether layer was then washed several times with water. Removal of the solvent left a green oil which was chromatographed on basic alumina. Elution with petroleum ether developed a blue band and a green band. The blue band was eluted with a 25:1 petroleum ether–methylene chloride solvent and afforded 30 mg. (73%) of 1-benzyl-3-chloroazulene as a blue-green oil. A cyclohexane solution showed λ_{max} in mμ (D_{max}) in the ultraviolet at 238 (0.43), 287 (1.04), 328 (0.04), 336 (0.07), 343 (0.09), 351 (0.13), 368 (0.12) with a shoulder at 293 (0.85), and in the visible at 629 (1.31), 660 (1.12), 689 (1.10), and 772 (0.39) with shoulders at 584 (0.91), 609 (1.16), and 730 (0.49). The infrared spectrum was essentially identical to that of the product obtained from the sodium borohydride reduction of the presumed [1-(3-chloroazulyl)]tropenium fluoroborate (below). The n.m.r. spectrum showed resonance peaks centered at 5.65 p.p.m. (saturated hydrogens), 2.89 p.p.m. (phenyl hydrogens), and for the azulene ring hydrogens at 2.52 p.p.m. (2-position), 2.54 p.p.m. (6-position), 1.89 and 1.78 p.p.m. (4- and 8-positions). The peaks for the 5- and 7-hydrogens were partially covered by the large phenyl hydrogen peak and the centers for these could not be determined.

Reaction of Presumed [1-(3-Chloroazulyl)]tropenium Fluoroborate (IV) with Sodium Borohydride.—Freshly chromatographed 1-tropenyl-3-chloroazulene (117 mg., 0.463 mmole) and triphenylmethyl fluoroborate (149 mg., 0.452 mmole) were allowed to react in the same manner as described above. The acetonitrile was removed (rotary evaporator) and the residue was subjected to a pressure of *ca.* 0.3 mm. (vacuum pump) for several minutes. The almost black crystalline material was then triturated with two 50-ml. portions of dry petroleum ether, a 50-ml. portion of dry ether, and a further 50-ml. portion of petroleum ether. The last two extracts were almost colorless. Removal of the solvent from the combined triturates and chromatography of the residue gave 22.5 mg. (21%) of triphenylmethane, 61 mg. of 1-triphenylmethyl-3-chloroazulene (isolated and characterized as described above), and 7 mg. of a green oil.

The brown, semicrystalline residue was triturated with methylene chloride and the green solution decanted from undissolved tropenium fluoroborate (identified as previously described). The methylene chloride was removed *in vacuo* and about 20 ml. of dry acetonitrile distilled onto the residue. To the dark green solution which formed was added 15 mg. (0.396 mmole) of sodium borohydride. The color of the solution immediately turned to a dark blue, then to a lighter blue and finally to a blue-green, all within a few minutes. The reaction mixture was poured into water and the whole extracted with petroleum ether. Removal of the solvent from the extract left a blue-green oil which was chromatographed on basic alumina. Petroleum ether eluted 11.5 mg. of triphenylmethane and then two blue-green fractions. From the second fraction was obtained 11 mg. of a green oil. The first fraction was rechromatographed. Petroleum ether eluted an additional 3.5 mg. of triphenylmethane, and a blue band having a blue-green tail developed. The main portion of this band was removed with 20:1 petroleum ether–methylene chloride and afforded 36 mg. of a blue-green oil. Continued elution removed the trailing portion which gave an additional 11 mg. of the green oil obtained from the second blue-green fraction. This green oil and the one obtained from the petroleum ether trituration prior to reduction had essentially identical ultraviolet and visible spectra. A cyclohexane solution of each showed λ_{max} in mμ (D_{max}) in the ultraviolet at 240 (0.76), 283 (1.26), 288 (1.30), 295 (1.24), 300 (1.23), 354 (0.18), and 370 (0.18) with a shoulder at 347 (0.14), and in the visible at 630 (1.27), 660 (1.10), 690 (1.09), and 774 (0.39) with shoulders at 585 (0.93), 610 (1.14), and 735 (0.49). The infrared spectra of the two oils were slightly different. The ultraviolet, visible, and infrared spectra of both oils were very similar to those of 1-tropenyl-3-chloroazulene (III) and on this basis the oils are postulated to be tautomeric isomers of III. The elementary analysis was performed on the product isolated after reduction.

Anal. Calcd. for $C_{17}H_{13}Cl$: C, 80.79, H, 5.18. Found: C, 81.30; H, 5.55.

A cyclohexane solution of the blue-green oil (which was not analytically pure) exhibited λ_{max} in mμ in the ultraviolet at 239, 287, 328, 336, 343, 352, and 368 with a shoulder at 293 and in the visible at 630, 660, 690, and 773 with shoulders at 586, 610, and 732. A sample for analysis was obtained by taking a center cut of the band upon rechromatography and heating the recovered oil at 65° *in vacuo* (0.2 mm.) for 2 days. The infrared and n.m.r. spectra of this material were essentially identical to those of the product from the chlorination of 1-benzylazulene (above) and both are therefore indicated to be 1-benzyl-3-chloroazulene.

Anal. Calcd. for $C_{17}H_{13}Cl$: C, 80.79, H, 5.18. Found: C, 80.90; H, 5.48.

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Selective Catalytic Hydrogenation of Nitroölefins

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The objective of this study was the catalytic hydrogenation of a straight-chain and a cyclic conjugated 1-nitroölefin to the corresponding oximes. The formation of nitroalkane was also investigated. 1-Nitro-1-octadecene and 1-nitrocycloöctene were chosen as model compounds. Their convenient synthesis was reported recently.[1]

The examples of catalytic hydrogenation of nitroolefins to oximes reviewed in the literature[2,3] are limited to compounds of the nitrostyrene type. Hydrogenation of substituted nitrostyrenes[4] with palladium on carbon in pyridine gives the corresponding oximes. Phenylacetaldoxime[5] was obtained from 1-phenyl-2-nitroethylene if the hydrogenation was carried out with platinum catalyst in alcohol containing a small amount of acid; the use of alcohol without the acid[5,6] leads to 1,4-dinitro-2,3-diarylbutane. The conversion of conjugated nitroölefins to nitroöalkanes by catalytic methods using neutral media has been studied[7] for various types of nitroölefins.

Table I summarizes our data on selective hydrogenation of 1-nitrocycloöctene I to cycloöctanoneoxime II and nitrocycloöctane III and of 1-nitro-1-octadecene IV to stearaldoxime V and 1-nitroöctadecane VI.

All reactions were carried out with palladium-on-carbon catalyst using 1.3–4 wt. % palladium metal based on nitroölefin. 1-Nitrocycloöctene I was quantitatively converted into a 5:1 mixture of cycloöctanoneoxime II and cycloöctanone VII. Whether 1.0 or 0.5 mole of hydrogen chloride was used per mole of I

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