order to examine the feasibility of retaining the acetate protecting groups under detritylation conditions, hydrogen chloride gas was passed for 2 hr. at room temperature through a solution of 1.4 g. of the trityl ether diacetate VIb in 50 cc. of dry chloroform. The solvent was removed *in vacuo* and the residue was adsorbed from 1:1 hexane–benzene on 70 g. of Merck alumina. Elution with this solvent mixture gave 365 mg. of triphenylcarbinol, while benzene led to an oil and then to a crystalline solid (265 mg.). Crystallization from methanol–chloroform and from benzene produced needles, m.p. 290–294°, which were shown by mixture melting point determination, infrared comparison and analysis to be somewhat impure lactone diacetate XIIIb.

Anal. Calcd. for $C_{34}H_{50}O_6$: C, 73.61; H, 9.09; O, 17.31. Found: C, 73.52; H, 9.21; O, 16.88.

Further development of the chromatogram with benzene–ether (1:1) and crystallization of the resulting solid from methanol afforded 240 mg. of methyl **treleasegenate 3,21-diacetate (XIV)** as needles showing m.p. 224–228°, $[\alpha]_D$ +80°; $\lambda_{max}^{CHCl_3}$ 2.85, 5.77 and 8.0 μ.

Anal. Calcd. for $C_{35}H_{54}O_7$: C, 71.64; H, 9.28; O, 19.09. Found: C, 71.74; H, 9.26; O, 19.19.

Treleasegenic Acid 28 → 21-Lactone 3-Acetate 30-Trityl Ether (XVb).—The lactone XIIIa (1.3 g.) was heated on the steam-bath overnight with 3.0 g. of trityl chloride in 60 cc. of pyridine. The products were isolated with ether in the usual manner and chromatographed on 70 g. of Merck acid-washed alumina. Elution with hexane–benzene (1:1) gave 2.69 g. of triphenylcarbinol, while benzene and benzene–ether (9:1) removed 1.61 g. of oil, which appeared to be the desired lactone trityl ether XVa by infrared examination. For adequate characterization, this material was transformed into the acetate XVb, which crystallized from methanol–chloroform as needles, m.p. 213–216°, $[\alpha]_D$ +41°, $\lambda_{max}^{CHCl_3}$ 5.65, 5.76, 6.7 (triplet) and 7.95 μ.

Anal. Calcd. for $C_{61}H_{62}O_5$: C, 81.13; H, 8.27; O, 10.60. Found: C, 80.73; H, 8.35; O, 10.70.

Cleavage of this acetate trityl ether (1.3 g.) was performed with hydrogen chloride–chloroform exactly as described above for the trityl ether diacetate VIb and there was obtained in addition to 150 mg. of unchanged starting material XVb (m.p. 211–215°), 360 mg. of the lactone **3-monoacetate XVIa**, m.p. 300–304° (from methanol–chloroform), $[\alpha]_D$ +16°; $\lambda_{max}^{CHCl_3}$ 2.90, 5.65, 5.80 and 8.0 μ.

Anal. Calcd. for $C_{32}H_{48}O_5$: C, 74.96; H, 9.44; O, 15.60. Found: C, 74.60; H, 9.44; O, 16.21.

Δ^{12}-Oleanene-3β,21β-diol-30-al-28-oic Acid 28 → 21-Lactone-3-Acetate (XVIb) and Conversion to Methyl Machaerinate (XVIIa).—A solution of 250 mg. of the lactone 3-acetate XVIa in 40 cc. of acetone (distilled from potassium permanganate) was treated dropwise with 0.14 cc. of standard chromium trioxide–sulfuric acid reagent.[30] After 5 minutes, much water was added, the product was extracted with ether and chromatographed on 7.5 g. of alumina. Elution with benzene–ether (9:1) gave the aldehyde XVIb as needles (104 mg.) from hexane–benzene, m.p. 290–295°, $[\alpha]_D$ +42°; $\lambda_{max}^{CHCl_3}$ 5.60, 5.78 and 7.97 μ.

Anal. Calcd. for $C_{32}H_{46}O_5$: C, 75.26; H, 9.08. Found: C, 75.04; H, 9.01.

The aldehyde (90 mg.) was heated under reflux for 1 hr. with 8 cc. of diethylene glycol and 0.4 cc. of 85% hydrazine hydrate. Potassium hydroxide (0.4 g.) was added, the mixture was heated under reflux for 30 min., the condenser was removed and the temperature was allowed to rise to 205°. After heating under reflux for an additional 3 hr., water and hydrochloric acid were added, the precipitated acid was collected and methylated with diazomethane. Crystallization from aqueous methanol gave 50 mg. of methyl machaerinate (XVIIa)[31] of m.p. 229–232°, $[\alpha]_D$ +72°; identity with an authentic sample[10] was established by mixture melting point determination and infrared comparison.

Acetylation with acetic anhydride–pyridine gave methyl machaerinate diacetate (XVIIb), m.p. and mixture m.p. 275–278°, $[\alpha]_D$ +89°. The infrared spectrum was identical with that of an authentic specimen.[10]

(30) See K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, THIS JOURNAL, **75**, 2548 (1953).

(31) For comparison with methyl treleasegenate (Ib), 50 mg. of methyl machaerinate was boiled for 4 hr. with 10 cc. of 10% methanolic potassium hydroxide, diluted with water and extracted with ether. No neutral material was isolated, but acidification, extraction with ethyl acetate and crystallization afforded 38 mg. of machaerinic acid.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Azulenes. VIII.[1] 1- and 2-*t*-Butylazulene. Migration of the *t*-Butyl Group

BY WERNER HERZ

RECEIVED OCTOBER 3, 1957

2-*t*-Butylazulene has been synthesized from 2-*t*-butylindan by the diazoacetic ester method. Application of this procedure to 1-*t*-butylindan gave a mixture of 1- and 2-*t*-butylazulene, due to partial migration of the *t*-butyl radical, azulene and a small amount of a 1,3-disubstituted azulene, possibly 1,3-di-*t*-butylazulene.

Because the position of groups on the azulene nucleus determines the visible absorption spectrum,[2] investigations in the azulene series afford a unique and facile method for studying the migration of substituents on an aromatic ring. It was this circumstance which led to the discovery that in the dehydrogenation of guaiol with selenium, methyl group migration takes place from the 1- to the 2-position of the azulene nucleus.

Under the somewhat less rigorous conditions required by dehydrogenation with palladium–charcoal, migration of alkyl groups seems to be susceptible to steric factors. Thus, 1-methyl, 1-ethyl- and 1-isopropylazulene all have been prepared in pure form.[2] On the other hand, while no migration occurs in the preparation of 1,4,8-trimethylazulene,[3] replacement of the 1-methyl group by the bulkier isopropyl radical results in isopropyl group migration and formation of vetivazulene.[4,5] Similar results, apparently due to interference between isopropyl and methyl groups in position 1 and 8 of the azulene nucleus, were reported subsequently[6] in another series of compounds. Ukita and co-workers[7] also observed isopropyl group migration when the tertiary alcohol obtained from the reac-

(1) Paper VII, W. Herz, THIS JOURNAL, **78**, 1485 (1956).

(2) For a review, see M. Gordon, *Chem. Revs.*, **50**, 127 (1952).

(3) W. Herz, THIS JOURNAL, **74**, 1350 (1952).

(4) W. Herz, *ibid.*, **75**, 73 (1953).

(5) The same migration, but under very much milder conditions (dehydrogenation with chloranil of the product which results when 1-isopropylazulene is treated with excess methyllithium), has been observed recently by K. Hafner and H. Weldes, *Ann.*, **606**, 90 (1957).

(6) W. Herz and B. E. Cleare, THIS JOURNAL, **77**, 2318 (1955).

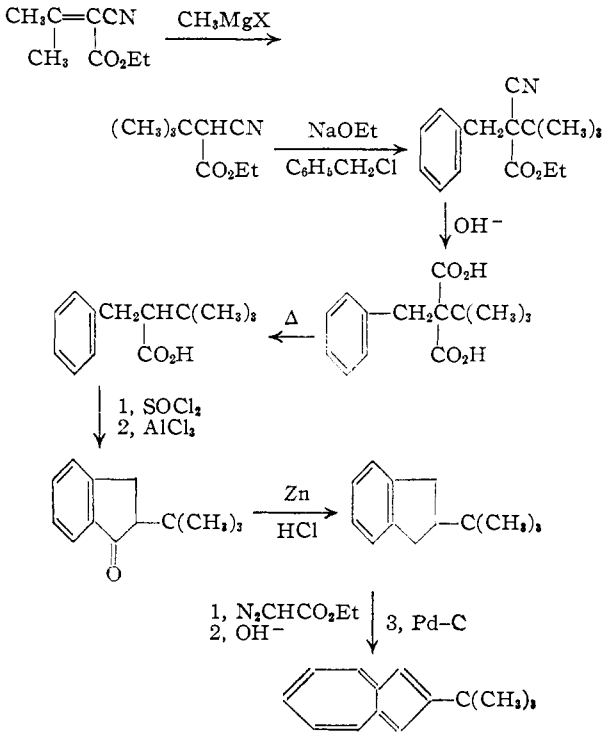
(7) T. Ukita, H. Watanabe and M. Miyazaki, *ibid.*, **76**, 4584 (1954).

tion of α-kessyl ketone with isopropylmagnesium iodide was dehydrogenated.

Of the monosubstituted azulenes synthesized thus far, only 1-phenylazulene has exhibited a tendency to rearrange under dehydrogenating conditions.[8] To which of several possible influences the migration of the phenyl group in this particular instance should be attributed cannot be decided on the basis of the available evidence. However, 1-benzylazulene does not rearrange under comparable conditions[9] and 1-benzhydrylazulene seems to be stable under the conditions of the Ziegler–Hafner azulene synthesis.[10]

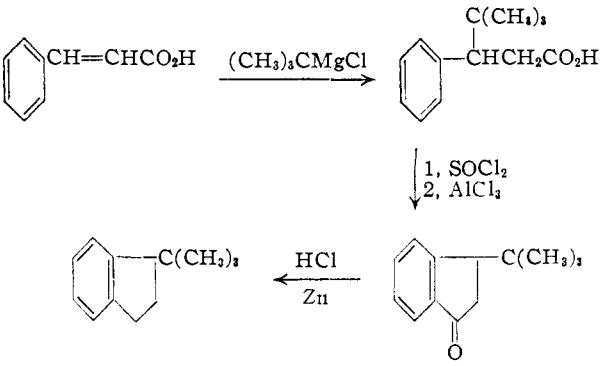
It appeared plausible that if steric factors play a role in these alkyl group migrations, an attempt at synthesis of 1-*t*-butylazulene might give rise to a certain amount of 2-*t*-butylazulene, due to the greater bulk of the *t*-butyl group as compared with that of the isopropyl radical. These expectations were borne out by the experimental facts described in this paper.

Authentic 2-*t*-butylazulene was synthesized by the series of reactions which need not be described in detail



2-*t*-Butylazulene, a violet solid, m.p. 70–71°, was characterized through its trinitrobenzene complex and exhibited the expected peaks in the visible and ultraviolet spectrum (Figs. 1 and 2).

When 1-*t*-butylindan, prepared as shown below, was subjected to treatment with diazoacetic ester and the resulting material hydrolyzed and dehydrogenated with palladium–charcoal, the azulene produced was obviously a mixture.



A combination of chromatography, partition between acid and organic phases[11] and fractional crystallization permitted the isolation and identification of three substances: (1) 2-*t*-butylazulene, whose identity was established by comparison with the authentic material (*vide supra*); (2) 1-*t*-butylazulene, a blue liquid, which was characterized through its trinitrobenzene complex and exhibited the expected peaks in the visible and ultraviolet spectrum (Figs. 1 and 2); and (3) azulene which was identified by its visible spectrum and conversion to the trinitrobenzene complex. A fourth, deep-blue fraction was isolated in very small amount, but could not be characterized sufficiently to permit identification. The visible spectrum, given in the Experimental section, indicated substitution in position 1 and 3 of the azulene nucleus and it is reasonable to assume that we were dealing with 1,3-di-*t*-butylazulene.[12]

The isolation of azulene and a 1,3-disubstituted azulene fraction (di-*t*-butylazulene?) in the present instance is analogous to the simultaneous formation of azulene and a 1,3-disubstituted azulene (dibenzylazulene?) from 1-benzylazulene on heating[9,13] where, however, no rearrangement to the 2-position was observed. Although the evidence gathered so far suggests it, it would be premature to conclude that 1,3-disubstitution, which probably involves an ionic process[14] and must be preceded or accompanied by dealkylation, and migration are entirely separate, independent reactions. It is conceivable that the products of dealkylation and disubstitution escaped detection during earlier work which reported only on products of migration.[4–8]

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation for which I express my thanks.

(8) Pl. A. Plattner, R. Sandrin and J. Wyss, *Helv. Chim. Acta*, **29**, 1604 (1946); Pl. A. Plattner, A. Fürst, M. Gordon and K. Zimmerman, *ibid.*, **33**, 1910 (1950).

(9) A. G. Anderson, Jr., and E. J. Cowles, THIS JOURNAL, **77**, 4617 (1955).

(10) K. Hafner, *Ann.*, **606**, 79 (1957).

(11) Pl. A. Plattner, E. Heilbronner and S. Weber, *Helv. Chim. Acta*, **32**, 574 (1949); **33**, 1663 (1950).

(12) The behavior of the corresponding naphthalene derivative is of interest. E. Illingworth and A. T. Peters, *J. Chem. Soc.*, 1603 (1951), state that 1-*t*-butylnaphthalene does not isomerize on heating except in the presence of certain catalysts. However, reference is made to unpublished work by N. G. Bromby, Thesis, Leeds University, 1941, who observed that 1-*t*-butyl-3,4-dihydronaphthalene was converted, on dehydrogenation with sulfur, to naphthalene, 2-*t*-butylnaphthalene and a small amount of oil whose picrate was identical with the picrate of authentic 1-*t*-butylnaphthalene.

(13) Under very much milder conditions, dealkylation as well as migration of an isopropenyl or isopropyl group was reported[7] as arising during the hydrogenation of 3-isopropenyl-5-guaiazulene.

(14) A. G. Anderson, Jr., J. A. Nelson and J. J. Tazuma, THIS JOURNAL, **75**, 4980 (1953).

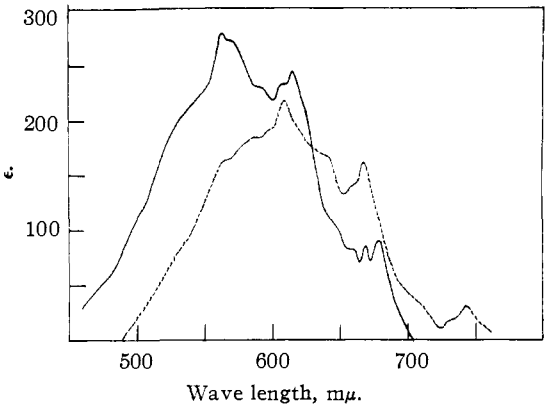


Fig. 1.—Visible spectrum: ----, 1-*t*-butylazulene; ———, 2-*t*-butylazulene in isoöctane solution.

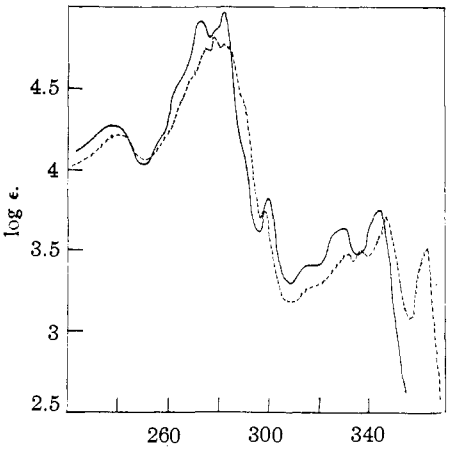


Fig. 2.—Ultraviolet spectrum: ----, 1-*t*-butylazulene; ———, 2-*t*-butylazulene in isoöctane solution.

Experimental[15]

β-*t*-Butylhydrocinnamic Acid.—The procedure given for the conjugate addition of *t*-butylmagnesium chloride to cinnamic acid[16] was modified in several minor details. The ether solution of the organic acids was concentrated *in vacuo*. The residual yellow solid, wt. 140 g., from a run using two moles of cinnamic acid, was recrystallized once from acetonitrile and once more from water–acetic acid. This resulted in 116 g. of pure product, m.p. 114–115°.

1-*t*-Butylindane.—The above acid was converted to 3-*t*-butylindanone by the method of Koelsch.[17] The dinitrophenylhydrazone was recrystallized from ethyl acetate and melted at 177°, scarlet plates or orange needles depending on speed of crystallization.

Anal. Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47; N, 15.21. Found: C, 62.06; H, 5.31; N, 15.6.

Clemmensen reduction of 103 g. of the indanone with 250 g. of freshly cleaned and amalgamated zinc, 100 ml. of water and 250 ml. of hydrochloric acid, accompanied by addition of three 100-ml. portions of hydrochloric acid at 6-hour intervals, resulted in isolation of 83 g. (87%) of 1-*t*-butylindane, b.p. 67–68° (1.4 mm.), $n^{22}D$ 1.5192.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.45; H, 10.28.

Ethyl Benzyl-*t*-butylcyanoacetate.—To a solution of 34.5 g of sodium in 1 l. of absolute ethanol was added 255 g. of ethyl *t*-butylcyanoacetate[18] with stirring, and then 189 g. of benzyl chloride. The mixture was refluxed with stirring for 18 hours, the alcohol was removed *in vacuo*, the residue cooled, diluted with water, and extracted with ether. The ether extracts were washed, dried, and distilled; forerun (mixture of starting materials) wt. 80 g., main fraction, b.p. 140–150° (2.5 mm.), wt. 280 g. (72%). The analytical sample boiled at 142° (2 mm.), $n^{23}D$ 1.4982.

Anal. Calcd. for $C_{16}H_{21}O_2N$: C, 74.14; H, 8.18. Found: C, 74.11; H, 7.95.

2-Benzyl-3,3-dimethylpropionic Acid.—A mixture of 33 g. of ethyl benzyl-*t*-butylcyanoacetate, 350 ml. of ethylene glycol, 20 ml. of water and 80 g. of potassium hydroxide was refluxed for six days in a copper flask, cooled, diluted with water and extracted with ether to remove partially hydrolyzed neutral material. Evaporation of the ether extract left no residue. The aqueous layer was acidified and extracted thoroughly with ether. The ether extracts were washed thoroughly, dried, and concentrated on the steam-bath. The residue crystallized on standing, wt. 16.5 g. (63%). The substance was purified by distillation, b.p. 132–138° (1 mm.), and crystallization from pentane in which it was quite soluble; m.p. 70°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.69; H, 8.69.

In a subsequent run, 144 g. of ester on refluxing for seven days in an analogous fashion, yielded only 46 g. (40%) of the acid and 22 g. (19%) of a neutral solid which on recrystallization from petroleum ether (b.p. 30–60°) melted at 89.5–90°. Analysis and the infrared spectrum (NH at 3505, 3300 cm.$^{-1}$, amide carbonyl at 1678 cm.$^{-1}$) of the colorless needles showed that this material was the amide.

Anal. Calcd. for $C_{13}H_{19}ON$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.81; H, 9.17; N, 7.25.

2-*t*-Butylindanone.—A mixture of 62 g. of the previous acid and 70 ml. of thionyl chloride was warmed on the steam-bath for several hours. The excess of thionyl chloride was removed *in vacuo*, the residue was dissolved in 250 ml. of thiophene-free benzene and 45 g. of anhydrous aluminum chloride was added in small portions. The mixture was allowed to stand for three hours and decomposed by pouring over ice–hydrochloric acid. The organic layer was extracted with ether. The ether layers were washed thoroughly with water, dilute base and again with water. Distillation furnished a fraction boiling in the range 113–120° (2.5 mm.), yield 47.5 g. (84%). Redistillation resulted in a b.p. of 113–115° (2.5 mm.), $n^{20}D$ 1.5332.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.69; H, 8.38.

The dinitrophenylhydrazone, orange-red needles from ethyl acetate, melted at 200–201°. A mixed m.p. with dinitrophenylhydrazine was depressed to 178–182°.

Anal. Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47. Found: C, 62.15; H, 5.30.

2-*t*-Butylindan.—Clemmensen reduction of 39 g. of 2-*t*-butylindanone in the manner described previously resulted in a main fraction, b.p. 75–82° (1 mm.), wt. 21 g., and a higher boiling fraction, b.p. 83–110° (1 mm.), wt. 8.5 g., which consisted largely of starting material and was used in another run. From a total of 86 g. of 2-*t*-butylindanone there was thus obtained, after repeated fractionation, 52 g. (77%) of 2-*t*-butylindan, b.p. 69–73° (0.8 mm.), $n^{22}D$ 1.5120, and 13 g. of higher-boiling material.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.38; H, 10.54.

2-*t*-Butylazulene.—Reaction of 52 g. of 2-*t*-butylindan with eight 10–12-g. portions of ethyl diazoacetate in the manner previously described[19] resulted in recovery of 19 g. of crude indan and isolation of 38 g. of highly colored ester, b.p. 130–180° (3.5 mm.). This was saponified by refluxing with 150 ml. of ethanol, 40 ml. of water and 25 g. of potassium hydroxide. The crude acid fraction, wt. 26 g., upon distillation furnished 17 g. of viscous dark-green material, b.p. 175–190° (2 mm.), which was dehydrogenated and de-

(15) M.p.'s and b.p.'s are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford, England. Ultraviolet and infrared spectra were determined by Miss N. Esquivel on Beckman model DKI and Perkin-Elmer model 21 spectrometers.

(16) J. H. Wotiz, J. S. Matthews and H. Greenfield, THIS JOURNAL, **75**, 6342 (1953). I am indebted to Mr. C. J. Ciotti who carried out this preparation.

(17) C. F. Koelsch, *ibid.*, **65**, 1640 (1943).

(18) E. R. Alexander, J. D. McCollum and D. E. Paul, *ibid.*, **72**, 4791 (1950).

(19) W. Herz, *ibid.*, **73**, 4923 (1951).

carboxylated by mixing with 3 g. of 10% palladium-on-charcoal and distilling over an open flame. The azulene was separated from the violet-blue distillate by extraction with 85% phosphoric acid; dilution of the phosphoric acid layer with water and extraction with petroleum ether gave, upon removal of solvent, 3.1 g. of solid violet-blue azulene. The non-azulenic fraction was dehydrogenated once more with 2 g. of 10% palladium-on-charcoal. An additional 1.1 g. of 2-*t*-butylazulene could be obtained in this way.

The azulene was converted to the trinitrobenzene complex; wt. of first crop 5.3 g. (the mother liquors yielded additional material which was not used in the purification procedure). Decomposition of the complex over alumina (solvent and eluent petroleum ether) yielded violet-blue needles which were sublimed at 70° (0.5 mm.) and melted at 70–71° with previous softening near 67°.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.23; H, 8.77. Found: C, 91.10; H, 8.71.

A solution of 7.9 mg. in 5 ml. of spectral grade isoöctane was used for determining the ultraviolet and visible spectrum. Maxima in the visible were at 679 mμ (ε 92), 668 (86), 651 (83), shoulders at 637 and 625, 614 (246), 607 (234), 594 (224), 580 (shoulder, ε 274), 570 (280), 562 (280), 551 (shoulder), 544 (224), 537 (212) and 527 (shoulder). Maxima in the ultraviolet occurred at 344 mμ (log ε 3.74), 328 (3.60), 316 (3.43), 300 (3.79), 282 (4.97), 275 (4.92) and 237 (4.30).

The trinitrobenzene complex was recrystallized three times from absolute ethanol. The rust-colored needles melted at 148.5–150° dec.

Anal. Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.41; H, 4.82; N, 10.6. Found: C, 60.64; H, 4.97; N, 10.5.

1-*t*-Butylazulene.—Treatment of 50.5 g. of 1-*t*-butylindan with eight 11-g. portions of ethyl diazoacetate resulted in recovery of 19 g. of crude starting material (b.p. up to 125° at 1 mm.) and 45 g. of product, b.p. 125–160° (2 mm.). This was hydrolyzed with 150 ml. of ethanol, 45 ml. of water and 25 g. of potassium hydroxide. The acid fraction, b.p. 170–180° (2 mm.), wt. 29.5 g., was dehydrogenated and decarboxylated by distilling over an open flame from 4 g. of 10% palladium-on-charcoal. The blue distillate (azulene mixture I) was collected at 80–130° (2 mm.)[20]; the forerun and residue were subjected to another dehydrogenation with palladium-on-charcoal and yielded more azulene mixture I, b.p. 80–130° (2 mm.). A higher boiling fraction, b.p. 130–190° (2 mm.), which appeared to be more violet was collected separately (azulene mixture II).

The combined fractions of b.p. 80–130° (2 mm.) were percolated through an alumina column (solvent and eluent petroleum ether). The first colorless eluate yielded a viscous high-boiling fraction, wt. 1.9 g. The color of the azulene which was eluted subsequently changed gradually from blue to blue-violet. The last more dilute fraction was collected separately and evaporated to dryness. The violet-blue crystalline residue was sublimed, but could not be induced to melt sharply, m.p. 65–70°. That this material was impure azulene (lit.[2] m.p. 99.5–100°) was shown by its visible absorption spectrum whose sharp bands and extinction coefficients (λ_{max} 698, 663, 634, 604, 580, 555, shoulders at 535 and 515 mμ; ϵ_{max} 115, 132, 299, 295, 329, 269) coincided almost exactly with the reported spectrum of azulene,[21] as well as by conversion to a trinitrobenzene complex, m.p. 165–166° (lit.[2] 166.5–167.5°).

The remaining azulene mixture I, wt. 6.3 g., was mixed with a solution of 7 g. of trinitrobenzene in 200 ml. of hot ethanol. On standing, there precipitated 6.5 g. of a mixture of trinitrobenzene complex and trinitrobenzene. On concentrating the filtrate to 30 ml., a second crop weighing 3.0 g. was obtained. The mother liquors were allowed to evaporate to small volume and filtered. The blackish solid residue was passed through an alumina column (solvent and eluent petroleum ether). The eluate portion containing the azulene was extracted repeatedly with 30-ml. portions of 85% phosphoric acid in which the azulene appeared to be relatively insoluble. The first three 30-ml. phosphoric acid portions were combined and diluted with water, the azulene was extracted with petroleum ether, the solvent removed and the azulene distilled in a sublimation apparatus. The blue-violet oil, wt. 0.106 g., was dissolved in 10 ml. of warm ethanol containing 75 mg. of trinitrobenzene, the mixture was heated to boiling and allowed to stand. The long, violet-black needles were recrystallized once more from ethanol and then melted at 123.5–124.5°. The spectrum identified this material as 1-*t*-butylazulene.

Anal. Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.41; H, 4.82; N, 10.6. Found: C, 60.23; H, 4.75; N, 10.6.

For spectral measurements 23.4 mg. of the complex was decomposed on a small alumina column (solvent and eluent spectral grade isoöctane). Maxima in the visible region occurred at 742 mμ (ε 30), 710 (shoulder, 42), 668 (165), 659 (143), 637 (shoulder, 168), 627 (shoulder, 184), 608 (220), 583 (186), 565 (shoulder, 164) and 535 (shoulder, 107). Bands in the ultraviolet were found at 362 mμ (log ε 3.55), 346 (3.72), 337 (3.51), 331 (3.50), 298 (3.73), 284 (4.78), 278 (4.81) and 274 (4.75).

The first two crops of trinitrobenzene complex from azulene mixture I were combined and decomposed by passage through an alumina column (eluent petroleum ether). The violet-blue eluate was concentrated on the steam-bath, but did not solidify (azulene mixture III). A 0.35-g. portion of this material in 10 ml. of ethanol was mixed with 0.4 g. of trinitrobenzene in 10 ml. of ethanol, heated and allowed to cool. After two recrystallizations from ethanol, the rust-colored needles melted at 150.5–151°, no depression on mixing with trinitrobenzene complex of authentic 2-*t*-butylazulene. Decomposition of the complex on an alumina column gave a solution whose visible spectrum was identical with the visible spectrum of authentic 2-*t*-butylazulene.

Similarly, azulene fraction II, after percolation through an alumina column, was converted to the trinitrobenzene complex. Two recrystallizations from ethanol furnished crystals of m.p. 146.5–147.5° (the lower m.p. may be due to slight contamination by other azulenes). The visible spectrum of the azulene recovered by decomposition of the complex was identical with the visible spectrum of authentic 2-*t*-butylazulene.

A sample of azulene mixture III was chromatographed over a large amount of alumina. The initial drops of azulene eluate appeared to be pure blue, rather than blue-violet, and were collected separately. The comparative sharpness of the bands in the visible spectrum of this material indicated a reasonable degree of purity; maxima were observed at 774, 690 (center of a relatively broad band with indications of sub-peaks near 680 and 700 mμ), 662 (shoulder), 634, 631 (strongest band), 604 and 579 mμ (shoulders). These maxima are characteristic of 1,3-disubstituted azulenes. Evaporation of the solvent left 21 mg. of a blue oil which was mixed with 25 mg. of trinitrobenzene in 2 ml. of warm ethanol. On chilling there separated violet-black needles, m.p. 101–112°, mixed with crystals of trinitrobenzene. Because of the relatively great solubility of this complex in ethanol, it was not possible to recrystallize this material to a constant sharp m.p.

TALLAHASSEE, FLA.

(20) The phosphoric acid extraction procedure was not used, in order to minimize possible migration of the *t*-butyl group under the influence of an acid catalyst.

(21) Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910 (1947).