

Communications TO THE EDITOR

Reaction of Azulene with *N*-Nitrosoacetanilide, Phenylazotriphenylmethane, and Benzoyl Peroxide

Sir:

Preliminary studies of the reaction of azulene with *N*-nitrosoacetanilide (I), phenylazotriphenylmethane (II), and benzoyl peroxide (III) have afforded quite novel results. Treatment of azulene with I in dry benzene at 3° [reported to give 15% of 1-phenylazulene (IV)¹] produced some (2.3%) of IV (identified by ultraviolet, visible, and infrared spectra) but mainly (19%) 1-phenylazoazulene (V), m.p. and mixed m.p. 118–120°,² (also identified by its infrared spectrum) plus ca. 60% of unreacted azulene. Reaction at 10° gave 5.4% of IV and 13% of V; at 15°, 1.3% of IV and 33% of V (ca. 40% recovered azulene). With the solvent benzene plus methanol with dissolved sodium acetate at 10° the yields were of the same order of magnitude (ca. 3% of IV, 20% of V, and 60% azulene). With the solvent methanol containing sodium acetate at 10°, V was still obtained (20%) but 1% or less of IV and ca. 10% of azulene. In all runs a black, crystalline, high melting (>360°) substance and a red, noncrystalline product of unknown identity were isolated in low yield.

Reaction of azulene with II³ in benzene under reflux gave less than 1% of IV and 2.4% of 1-triphenylmethylhydrazoazulene (VI) as blue crystals, m.p. 115–116°, along with triphenylmethane (34%). The identity of VI rests on the reasonable assumption of substitution in the 1-position, analysis (Calcd. for C₂₉H₂₄N₂: C, 86.96; H, 6.04; N, 7.0. Found: C, 87.26; H, 6.36; N, 6.78) and absorption spectra. The ultraviolet and visible spectra of VI (λ_{\max} in cyclohexane at 237, 272, 276, 282, 297 (shoulder), 327, 342, 353, 535, 558, 580, 606, 632, 662, and 700 m μ) were markedly different than those to be expected for the corresponding azo compound (which would resemble V).

From thermal (65–75°) decomposition of purified benzoyl peroxide in the presence of azulene (benzene solvent; nitrogen atmosphere) for 2 hr. was obtained a blue oil (18%), difficult to purify, which displayed carbonyl absorption (5.8 μ) and λ_{\max} (cyclohexane) at 236, 272 (shoulder) 276, 281, (shoulder), 296 (shoulder), 342, 368, 537 (shoulder),

558 (shoulder), 580, 605, 631, 662, 679, and 735 m μ and is most probably 1-azulylbenzoate (VII) (Calcd. for C₁₇H₁₂O₂: C, 82.24; H, 4.87. Found: C, 82.69; H, 5.19). Some azulene (30%) was recovered but no other products (1-phenylazulene was expected) could be isolated. That VII could not be 1-benzoylazulene (VIII) was shown by preparation of the latter (Calcd. for C₁₇H₁₂O: C, 87.90; H, 5.21. Found: C, 87.68; H, 5.23) from azulene, benzoyl chloride, and stannic chloride. VIII formed purple crystals, m.p. 111–112°, and exhibited absorption similar (*e.g.*, a carbonyl peak at 6.2 μ) to that of 1-acetylazulene.²

V is presumably formed *via* benzenediazoacetate (IX) (from rearrangement of I) by (a) homolytic cleavage of IX to produce Ar-N=N·, (b) ionization of IX to give ArN₂⁺ or (c) displacement of OAc[−] from IX by the nucleophilic azulene. If by (a), then V should have been formed from azulene and II (which gives Ar-N=N· initially). It was not. If by (b), a change in the polarity of the solvent medium should have had a marked effect. It did not. These preliminary results thus favor route (c).

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Preparation and Proof of Structure of 7,8-Dihydroabietic Acid

Sir:

Although several dihydroabietic acids have been described,¹ many are of doubtful homogeneity, and in no case has a rigorous proof of structure been offered. We wish now to report the preparation and proof of structure of 7,8-dihydroabietic acid.

Reduction of the di-*n*-amyl amine salt of abietic acid by treatment with lithium in ether and liquid ammonia followed by addition of ethanol gave in 25–30% yield pure 7,8-dihydroabietic acid (I), m.p. 197.0–197.5°,² $[\alpha]_D^{25} -24.7^\circ$. (*Anal.* Calcd. for C₂₀H₃₂O₂: C, 78.8; H, 10.63. Found: C, 78.41; H, 10.73.) Homogeneity of this dihydroabietic acid was demonstrated by conversion to the di-*n*-

(1) See J. L. Simonsen, *The Terpenes*, Sec. Ed., Vol. III, Cambridge Univ. Press, Cambridge, 1952, pp. 407–410 and 417–418.

(2) All reported melting points are uncorrected and were taken in nitrogen-filled sealed capillaries. Specific rotations were taken in 1% absolute ethanol using the sodium D line.

(1) H. Arnold and K. Pahls, *Ber.*, **89**, 121 (1956).

(2) A. G. Anderson, J. A. Nelson, and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953).

(3) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953).