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 II[3] 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 $C_{29}H_{24}N_2$: 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 $\underline{237}$, $\underline{272}$, $\underline{276}$, $\underline{282}$, 297 (shoulder), 327, 342, 353, 535, 558, $\underline{580}$, $\underline{606}$, $\underline{632}$, 662, and 700 mμ) 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 (5.8μ) and λ_{max} (cyclohexane) at $\underline{236}$, $\underline{272}$ (shoulder) $\underline{276}$, $\underline{281}$, (shoulder), 296 (shoulder), 342, 368, 537 (shoulder), $\underline{558}$ (shoulder), $\underline{580}$, $\underline{605}$, $\underline{631}$, $\underline{662}$, $\underline{679}$, and 735 mμ and is most probably 1-azulylbenzoate (VII) (Calcd. for $C_{17}H_{12}O_{12}$: 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 $C_{17}H_{12}O$: 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 6.2μ) 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 $ArN_2^{\oplus}$ or (*c*) displacement of $OAc^{\ominus}$ 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*).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASH.

ARTHUR G. ANDERSON, JR.
GERALD M-C. CHANG

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

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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°. (*Anal.* Calcd. for $C_{20}H_{32}O_2$: 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*-

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[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.

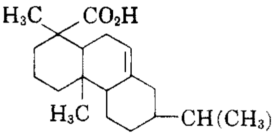
amyl amine salt, recrystallization of the salt to constant properties, m.p. 117–118°, $[\alpha]_D^{25}$ $-20.4°$, and regeneration of the dihydroabietic acid with unchanged properties. Catalytic hydrogenation of 7,8-dihydroabietic acid over platinum led to the absorption of 1.05 moles of hydrogen and production of a tetrahydroabietic acid melting sharply without purification at 185.5–186.0°, $[\alpha]_D^{25}$ $-2.3°$. (*Anal.* Calcd. for $C_{20}H_{34}O_2$: C, 78.70; H, 10.83. Found: C, 78.33; H, 11.11.) Treatment of 7,8-dihydroabietic acid with an excess of monoperphthalic acid in ether led to consumption of 1.03 moles of peracid and formation of a crystalline epoxide, m.p. 167.0–168.5°.

Ozonolysis of 7,8-dihydroabietic acid in *n*-heptane solution and decomposition of the ozonide by bubbling air through its basic aqueous-alcoholic solution gave a crude acidic product. Treatment of the crude acid with acetic anhydride at reflux led to the isolation of a non-crystalline cyclic anhydride (II), showing infrared absorption maxima at 5.51 and 5.74 μ (anhydride) and at 5.82 μ (ketone). [*Anal.* Calcd. for $C_{10}H_{20}O_4$: C, 71.82; H, 9.04; sapon. equiv., 167.2; mol. wt., 334.4. Found: C, 72.26; H, 9.53; sapon. equiv., 169.5; mol. wt. (Rast), 336.]. Formation of this cyclic anhydride is consistent only with structure I for our dihydroabietic acid.

Treatment of 7,8-dihydroabietic acid with nitrosyl chloride gave a crystalline α-chloro oxime, m.p. 176.0–176.5°, which on dehydrohalogenation with pyridine gave an α,β-unsaturated oxime, m.p. 192.5–193.0°, λ_{max} 235 mμ, ε 6,600. (*Anal.* Calcd. for $C_{20}H_{31}NO_3$: N, 4.20. Found: N, 4.12). Acid hydrolysis of this oxime gave an α,β-unsaturated ketone (III), m.p. 156.5–157.0°, λ_{max} 249 mμ, ε 6,400. This value of the ultraviolet absorption maximum is in precise agreement with Woodward's Rule for structure III.

Treatment of 7,8-dihydroabietic acid with hydrogen bromide in glacial acetic acid gave 13,14-dehydrotetrahydroabietic acid (IV), m.p. 174–175°. (*Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.8; H, 10.63. Found: C, 78.41; H, 10.73). Treatment of IV with nitrosyl chloride gave a blue nitrosochloride, m.p. 140.0–140.5° (dec.), which readily lost the elements of nitrosyl chloride on heating with regeneration of IV.

Treatment of 7,8-dihydroabietic acid with cold, concentrated sulfuric acid led to the formation of an oil which was shown to be a mixture of the well-known γ-lactone (V)[3] and an isomeric δ-lactone, probably VI. The mixture of lactones showed infrared absorption at 5.68 μ (γ-lactone) and at 5.87 μ (δ-lactone). Treatment of the lactone mixture with refluxing butanolic potassium hydroxide led to hydrolysis of the γ-lactone with formation of a crystalline hydroxy acid, m.p. 164.5–166.0°, undoubtedly identical with that of Ruzicka.[4] On heating this hydroxy acid at its melting point, there was obtained the pure γ-lactone, m.p. 130–131°, which did not depress the melting point of an authentic specimen. (*Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.80; H, 10.60. Found: C, 78.65; H, 10.60.) The residual unhydrolized δ-lactone could not be obtained crystalline; $[\alpha]_D^{25}$ $-43.0°$. (*Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.80; H, 10.60. Found: C, 78.44; H, 10.64.) Construction of Stuart-Briegleb models indicates that although the δ-lactone (VI) can be formed without distortion of normal bond angles, the carbonyl group is extremely hindered. The lactones V and VI were formed in an approximate ratio of 2:3. Treatment of the isomeric 13,14-dehydrotetrahydroabietic acid with cold, concentrated sulfuric acid gave an apparently identical mixture of lactones.



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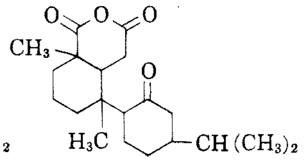

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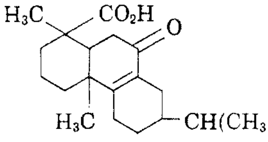

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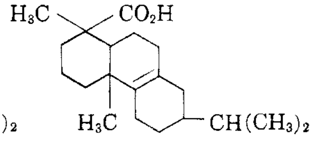

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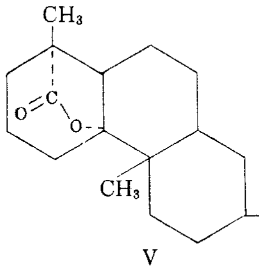

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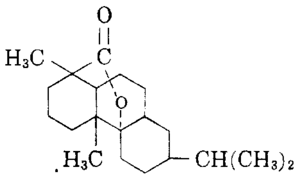

VI

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Department of Chemistry
Emory University
Emory University, Ga.

E. Earl Royals
William C. Bailey
Robert W. Kennedy

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