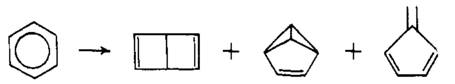
as a complement to our investigation of the vacuum ultraviolet photolysis of benzene vapor.[13] We should like now to present the results of this study.

Neat liquid benzene was irradiated with the emission from a microwave-powered oxygen discharge (bands extending from ~2000 to ~1650 Å).[14] The resulting product mixture, in contrast to the complex photolysate of the vapor-phase reaction,[13,15] was remarkably simple, with only three volatile products being observed. These have been identified as Dewar benzene (III), benzvalene (I), and fulvene (II).



III I II

Fulvene,[16] Dewar benzene,[17] and benzvalene[2] were prepared independently by known methods, and their chromatographic properties were compared with those of the photoproducts. Molecular weights were obtained for the photoproducts by mass spectral parent ion analysis using a gas chromatograph–mass spectrometer[18] combination in which part of the effluent from the gas chromatograph passed directly into the mass spectrometer. In each case, the parent ion corresponded to mol wt 78. These results are summarized in Table I. In addition, the product ultimately identified as Dewar benzene was isolated, along with a small amount of benzene, by preparative gas chromatography. When heated in pyridine, the photoproduct reverted to benzene.[19] Biphenyl was also formed in small amounts, and irradiation for more than 40 min (~4 × 10^{18} quanta) produced noticeable polymer on the lamp window. No fragmentation products were observed. An attempt was made to detect prismane[20] using highly basic gas chromatography columns,[11a] but no evidence for this compound was found.

Table I. Chromatographic Properties of Photoproducts and Known Compounds

Compd	Retention time relative to benzene		
	UCON (40°)	Squalane (30°)	DDP–TEA (25°)[b]
Dewar benzene	0.45	0.63	
Photoproduct **1**	0.45	0.61	0.45[c]
Fulvene	0.90	0.77	*d*
Photoproduct **2**	0.89	0.77	*d*
Benzvalene	*a*	*a*	0.80
Photoproduct **3**	*a*	*a*	0.80

[a] Benzvalene does not elute from these columns. [b] Didecyl phthalate–triethanolamine. To our knowledge, this is the only chromatographic system which does not decompose benzvalene.[2] [c] Has not been determined for authentic Dewar benzene. [d] Fulvene is decomposed on this column.

The relative concentrations of the photoproducts were found to be about 1:2:5 (Dewar benzene:fulvene: benzvalene), but it is possible that some of the fulvene arises from the acid-catalyzed rearrangement of benzvalene.[21] This ratio corresponds to quantum yields (oxygen actinometry[22]) of $\Phi = 0.006$ (Dewar benzene), 0.012 (fulvene), and 0.03 (benzvalene). The low quantum yield for this reaction suggests that radiationless transitions to the ground electronic state may be important in this system, since neither fluorescence nor phosphorescence is significant when neat liquid benzene is irradiated in the vacuum ultraviolet.[23]

---

(13) H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **89**, 162 (1967).

(14) A similar lamp has been described elsewhere: H. R. Ward, *ibid.*, **89**, 2367 (1967).

(15) (a) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *ibid.*, **88**, 3698 (1966); (b) L. Kaplan and K. E. Wilzbach, *ibid.*, **89**, 1030 (1967).

(16) (a) J. Thiec and J. Wiemann, *Bull. Soc. Chim. France*, 177 (1956); (b) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 1409 (1960).

(17) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963).

(18) The mass spectrometer used in this study was purchased with funds supplied by the National Science Foundation.

(19) Dewar benzene is known to isomerize to benzene under these conditions.[17]

(20) Tetracyclo[2.2.$0^{2,6}$.$0^{4,5}$]hexane.

(21) The fulvene:benzvalene ratio appears to be a strong function of the acidity of the lamp surface. A base-washed surface results in a predominance of fulvene, while a base-*coated* surface gives the results reported above. The Dewar benzene is apparently not affected by these changes.

(22) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 782, and references contained therein.

(23) C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, **39**, 1645 (1963).

(24) NASA Trainee, 1965–1967.

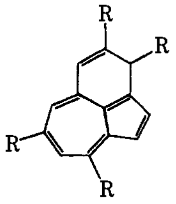
Harold R. Ward, John S. Wishnok[24]
Metcalf Research Laboratories, Brown University
Providence, Rhode Island 02912

Received November 13, 1967

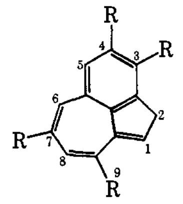
An 8H-Azuleno[1,8-*bc*]thiophene Derivative

Sir:

Hafner and Schaum[1] have recently reported that a cyclization reaction which should have yielded the tetramethyl derivative of an azulenocyclohexadiene (**1a**) gave instead 3,4,7,9-tetramethyl-2H-benz[*cd*]-azulene (**2a**). Boekelheide and Smith[2] prepared the parent system **2b** and, noting the relative ease of formation of the anion, raised the question of tautomerism and the position of the "extra" hydrogen in the molecule. They established the structure as **2b** in contrast to other tautomers such as **1b** on the basis of the similarity of its ultraviolet spectrum (λ_{max} 427 mμ) to that of heptafulvene. Tautomer **1b**, which is an azulene, should have its principal maximum at a wavelength longer than 500 mμ.



1



2

a, R = CH_3; **b**, R = H

These data clearly show that the benzoheptafulvene system **2** is more stable than the azulenocyclohexadiene tautomer **1**. Delocalization energies (Table I) calculated by us using simple HMO and ω-variation, self-consistent-field methods[3] suggest a relative order of stabilities consistent with the experimental observations.

---

(1) K. Hafner and H. Schaum, *Angew. Chem. Intern. Ed. Engl.*, **2**, 95 (1963).

(2) V. Boekelheide and C. D. Smith, *J. Am. Chem. Soc.*, **88**, 3950 (1966).

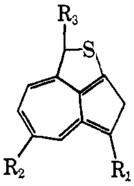
(3) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 115.

Table I. Delocalization Energies Calculated with the HMO and ω-Variation, Self-Consistent-Field Technique[a]

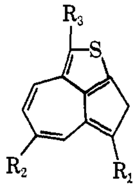
Molecule	HMO DE	ω-Technique DE
1b	3.826β	3.729β
2b	3.859β	3.840β
3a[b]	3.664β	3.574β
4a[b]	3.351β	3.339β

[a] Reference 3. [b] The S atom was treated according to the technique of H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

Heterocycles which are analogs of nonbenzenoid aromatic hydrocarbons have been of interest to us for some time. In view of the lower resonance energy of thiophene (28–31 kcal/mole)[4] relative to that of benzene (36 kcal/mole), a heterocyclic analog of **2**, in which a sulfur atom has replaced the C_3–C_4 ethylenic linkage, might be anticipated to exist as the azulenodihydrothiophene isomer **3a** in preference to the heptafulvenothiophene isomer **4a**. This expectation is supported by the delocalization energies calculated for **3a** and **4a** (Table I).



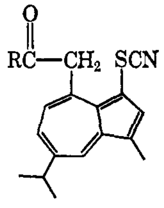
3



4

a, $R_1 = R_2 = R_3 = H$
b, R_1 = Me; R_2 = *i*-Pr; $R_3 = C_6H_5CO$
c, R_1 = Me; R_2 = *i*-Pr; R_3 = *p*-BrC_6H_4

It seemed likely that the thiocyanoketone **5a**, which had previously been used to prepare the azuleno[1,8-*bc*]thiapyran ring system,[5] could be converted to the cyclic sulfide **3b** by treatment with base. Treatment of **5a** with a tertiary amine in a polar organic solvent (*e.g.*, dimethyl sulfoxide) or with potassium hydroxide in methanol–ether solution gave a red, crystalline solid, mp 109.5–111°, in good (70–90%) yield. The elemental analysis (*Anal.* Found: C, 79.52; H, 5.96; S, 9.37) and mass spectral molecular weight (332.12) of this substance are in accord with a molecular formula



5a, R = C_6H_5
b, R = *p*-BrC_6H_4

of $C_{22}H_{20}OS$ (one molecule of **5** minus the elements of HCN). However, the carbonyl band in the infrared at 6.11 μ and the $\lambda_{\max}^{\mathrm{CHCl_3}}$ at 504 mμ in the visible are strong evidence that the compound is not the expected **3b**. **3b** should exhibit a normal carbonyl absorption at $\sim$5.9 μ and have a visible spectrum very similar to that of 3,8-dimethyl-5-isopropyl-1-methylthioazulene[6] ($\lambda_{\max}$ 654 mμ). The nmr spectrum shows approximately the pattern expected for **3b**. However, the chemical shifts are at higher fields than normally observed for aromatic azulene derivatives, and the broad peak at τ 6.78, which might be assigned to the proton adjacent to the carbonyl group, contains the correct area for two protons. The spectral data are in complete agreement with structure **4b**, 2-benzoyl-5-isopropyl-7-methyl-8H-azuleno-[1,8-*bc*]thiophene.[7]

Additional support of the proposed structure has been obtained from an X-ray crystallographic investigation[8] of a bromine derivative (**4c**), prepared by treating **5b** with pyridine in a similar reaction. Crystals of **4c** belong to the monoclinic system with cell constants of a = 9.063, b = 10.807, c = 19.368 Å, and β = 102.38°; space group $P2_1/n$. Full three-dimensional data have been collected with Mo Kα radiation on a General Electric automatic diffractometer. The R factor is presently 0.09. All hydrogen atoms have been located and the determination is in complete agreement with structure **4c**.

The reaction mechanism leading from **5a** to **4b** most probably proceeds *via* **3b** as a labile intermediate followed by a prototropic rearrangement to **4b**. It is interesting to note that our results show that **4b** is more stable than **3b**; this is in opposition to expectations based on the delocalization energies calculated for **4a** and **3a** (Table I). Most likely, the benzoyl substituent on C_2 is responsible for this discrepancy in that it is able to interact with the π electrons in the remainder of the molecule only in structure **4b**, and not in **3b**. Evidence for strong conjugative interaction between the carbonyl group and the π system is provided by the rather long wavelength position, 6.11 μ (1637 cm^{-1}), of the carbonyl band in the infrared spectrum of **4b**.

Acknowledgment. We wish to thank the National Science Foundation for financial support and the Trustees of the California State Colleges for a Special Leave for Research to L. L. R. We also wish to thank Dr. Harmon Brown of Varian Associates for the mass spectral data and Professor James M. Stewart, University of Maryland, for the use of X-ray diffraction facilities.

(4) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 99; L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 303.

(5) L. L. Replogle, K. Katsumoto, and T. C. Morrill, *Tetrahedron Letters*, 1877 (1965).

(6) L. L. Replogle, R. M. Arluck, and J. R. Maynard, *J. Org. Chem.*, 30, 2715 (1965).

(7) The τ 6.78 absorption was assigned to the C_8-methylene group.

(8) H. L. Ammon and P. H. Watts, Jr., unpublished work.

Lanny L. Replogle, Kiyoshi Katsumoto
Department of Chemistry, San Jose State College
San Jose, California 95114

Herman L. Ammon
Division of Natural Science, University of California
Santa Cruz, California 95060

Received November 17, 1967

The Structure of Actinobolin

Sir:

In a previous paper[1] the consequence of acid-induced cleavage of the antibiotic actinobolin was described. That information and the evidence derived from the

(1) M. E. Munk, C. S. Sodano, R. L. McLean, and T. H. Haskell, *J. Am. Chem. Soc.*, **89**, 4158 (1967).