Preparation of 2-Alkoxyimino Aldehydes and Ketones by the Oxidation of Alkoxyiminoalkanes with Selenium Dioxide[1]

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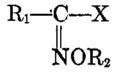
Two 2-alkoxyiminoaldehydes have been prepared in low yield by reduction of the corresponding 2-alkoxyiminoacyl halides with lithium tri-*tert*-butoxyaluminohydride.[3] 2-Alkoxyimino ketones have not been reported, however.

TABLE I
COMPOUNDS PREPARED BY THE SeO_2 OXIDATION OF ALKOXYIMINOALKANES



$R_1-C(=NOR_2)-X$

Registry no.	R_1	R_2	X	Bp, °C (Torr)	Refractive index	Yield, %	Composition	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
32349-36-3	Ph	Me	CHO	63–65 (0.035)	$n^{20}D$ 1.5455	49	$C_9H_9NO_2$[a]	54.09	5.41	24.54	54.32	5.33	24.92
32349-37-4	Ph	Et	CHO	59–61 (0.002)	$n^{24}D$ 1.5380	60	$C_{10}H_{11}NO_2$[b]	56.41	5.98	23.93	56.65	5.68	23.85
32349-39-6	EtCO	Et	H	132–134	$n^{24}D$ 1.4318	33	$C_6H_{11}NO_2$	55.81	8.53	10.85	55.54	8.72	10.65

[a] Analyzed as semicarbazone ($C_{10}H_{12}N_4O_2$), mp 195°, registry no. 32382-33-5. [b] Analyzed as semicarbazone ($C_{11}H_{14}N_4O_2$), mp 175°, registry no. 32349-38-5.

Imine nitrogens in heteroaromatic systems like carbonyls cause adjacent methylenes to become oxidized to aldehydes or ketones by SeO_2. In these systems, however, the corresponding acid derivatives have a great propensity to form.[4,5]

In an effort to develop a general procedure for introducing a carbonyl adjacent to an alkoxyimino function, *O*-alkyl oximes were treated with SeO_2. Ethers (methyl and ethyl) of acetophenone oxime were oxidized to the desired aldehydes in good yield. The corresponding free oximes produced tar. The *O*-ethyl ether of butyraldoxime was readily oxidized to 2-oxobutyraldoxime *O*-ethyl ether. The compounds prepared are shown in Table I with pertinent physical and analytical data.

When the *O*-ethyl ethers of purely aliphatic compounds like acetone and 3-methyl butanone were treated with SeO_2 in ethanol they yielded mainly ethyl esters of the corresponding 2-alkoxyimino acids. Spectral and chemical evidence confirmed the presence of the esters (see Experimental Section). Ester formation apparently results from an acid-catalyzed condensation between the carboxylic acids generated and the solvent (ethanol).

In the case of acetone oxime *O*-ethyl ether, running the reaction without solvent or in a mixture of dioxane and water produced no aldehyde.

Experimental Section

General Procedure.—The optimum conditions varied from compound to compound, but the general procedure involved heating equimolar quantities of selenium dioxide and the oxime ether in a solution of *p*-dioxane and water (8:1) at reflux for 4.5 hr. Filtration of the reaction mixture to remove selenium was followed by removal of solvent and distillation of the residue.

Characterization of Esters.—When acetone oxime *O*-ethyl ether was treated with selenium dioxide in alcohol–water at reflux the product, bp 70–72° (15 Torr), $n^{26}D$ 1.4540, showed no aldehydic proton in the nmr. It did show a weak carbonyl bond at 1735 cm^{-1} (film) in the ir and a parent ion at m/e 159 in the mass spectrum. Basic hydrolysis of the product yielded a white solid which was identified as 2-ethoxyiminopropionic acid, mp 68–70° (lit.[6] 68–70°).

In like manner ethyl 2-ethoxyimino-3-methylbutanoate, bp 64–66° (13 Torr), $n^{26}D$ 1.4339, was obtained from 2-ethoxyimino-3-methylbutanone. No aldehydic proton was observed in the nmr, but there was a weak carbonyl at 1730 cm^{-1} (film) in the ir and a parent ion at m/e 187 in the mass spectrum.

Registry No.—SeO_2, 7446-08-4.

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[1] Abstracted in part from the Ph.D. dissertation of L. A. S., University of Illinois, 1971.

[2] Department of Medicinal Chemistry, University of Kansas, Lawrence, Kans.

[3] D. A. Coviello and W. H. Hartung, *J. Org. Chem.*, **24**, 1611 (1959).

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Hückel Molecular Orbital Calculations of the Index of Aromatic Stabilization of Polycyclic Conjugated Molecules[1,2]

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In recent years there have been various attempts[3–7] to improve the predictive power of the HMO method originated by Hückel[8] in 1931. Here we would like

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[1] Presented in part at the Meeting of Croatian Chemists, Zagreb, Croatia, Yugoslavia, Feb 1971.

[2] This note was based upon B.S. theses submitted by M. Milun and Ž. Sobotka in partial fulfillment of the requirements for the B.S. degree at the Croatian University, Zagreb, 1971.

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[5] J. Kruszewski and T. M. Krygowski, *Tetrahedron Lett.*, 319 (1970).

[6] T. M. Krygowski, *ibid.*, 1311 (1970).

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to report a different and more realistic criterion for aromaticity. Namely, one of the long-standing problems is concerned with Hückel delocalization energies (DE), which estimated in the standard manner[9] are not always a reliable guide of aromaticity. For example, pentalene, a very unstable molecule showing no aromatic properties,[10,11] has a greater value of DE (2.46 β) than benzene (2.00 β). There are a number of other examples: heptalene, fulvene, fulvalene, heptafulvene, etc., which were all predicted to be aromatic on the grounds of their DE values being large, thus having a significant resonance stabilization. Such a prediction has been largely disproved by efforts to synthesize these compounds: heptalene has not been prepared[12] as yet, while fulvene, fulvalene, and heptafulvene were prepared,[13,14] but they undergo polymerization readily.

Therefore, we present here a new and simple criterion for aromaticity: the HMO index of aromatic stabilization (A_s). We define the index of aromatic stabilization as the difference between the HMO energy of a given conjugated molecule and the HMO energy of a corresponding classical structure. The HMO energy of the classical structure is equal to the sum of the "polyene" double bond energies and "polyene" single bond energies. "Polyene" bond energies can be obtained by considering linear conjugated polyenes. The general formula for a linear conjugated polyene is

$$CH_2{=}CH({-}CH{=}CH)_nH$$

A

Dewar presented evidence in several works[15-17] that bonds in classical polyenes[18] can be regarded as localized. Accepting this conclusion[19] one can write the total HMO energy for polyene A as

$$E_{\text{total}} = n(E_{C=C} + E_{C-C}) + E_{C=C}$$

where $E_{C=C}$ and E_{C-C} are "polyene" double and single bond energies, respectively. A plot of E_{total} *vs.* n should then be a straight line of slope ($E_{C=C} + E_{C-C}$) and intercept $E_{C=C}$. We have calculated HMO energies for polyenes from $n = 1$ to $n = 9$ and have found a linear relationship which led to the following "polyene" bond energies: $E_{C=C} = 2.00\ \beta$ and $E_{C-C} = 0.52\ \beta$.

Using these values we calculated the HMO index of aromatic stabilization for various conjugated hydrocarbons. These results are listed in Table I, which also contains, for comparison, the HMO delocalization energies and "resonance energies" (DRE) determined in the manner described by Dewar and coworkers[20-22] using a variant[23] of the SCF π-molecular orbital method.[24]

Table I

Delocalization Energies (DE), Indices of Aromatic Stabilization (A_s), and Dewar's Resonance Energies (DRE)

Compd	DE (in units β)[a]	A_s (in units β)	DRE, kcal/mol[b]
Benzene (**1**)	2.000	0.440	20.0
Naphthalene (**2**)	3.683	0.563	30.5
Anthracene (**3**)	5.314	0.634	36.9
Phenanthrene (**4**)	5.448	0.768	44.6
Chrysene (**5**)	7.192	0.952	57.3
Triphenylene (**6**)	7.274	1.034	61.2
Perylene (**7**)	8.245	0.965	60.4
Coronene (**8**)	10.572	1.212	81.3
Pyrene (**9**)	6.505	0.785	48.4
Styrene (**10**)	2.424	0.344	19.8
Biphenyl (**11**)	4.383	0.743	39.2
Azulene (**12**)	3.364	0.244	4.2
Pentalene (**13**)	2.456	−0.144	−6.5
Heptalene (**14**)	3.618	−0.022	−2.1
Fulvene (**15**)	1.466	−0.094	1.1
Heptafulvene (**16**)	1.994	−0.086	0.5
Fulvalene (**17**)	2.799	−0.321	2.5
Heptafulvalene (**18**)	4.004	−0.155	2.3
Cyclcobutadiene (**19**)	0.000	−1.040	−18.0[c]
Cyclooctatetraene (**20**) (planar)	1.657	−0.420	−2.6

[a] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965. [b] M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969); C. de Llano, Ph.D. Thesis, University of Texas, Austin, 1968. [c] M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *J. Amer. Chem., Soc*, **93**, 3437 (1971).

As seen from Table I, compounds **1-11** are predicted to be aromatic, all having large values of the A_s index. This is in agreement with their observed properties.[25] A number of nonbenzenoid hydrocarbons investigated in the present work are predicted to be nonaromatic, polyolefinic compounds, having negative A_s indices. This prediction agrees with their high degree of instability.[10-14]

The HMO delocalization energies, as it is clearly seen from Table I, do not differ between typically aromatic and nonaromatic molecules; the DE values, with the exception of cyclobutadiene (**19**), are very much alike for both classes of hydrocarbons. On the other hand, our results follow closely Dewar's resonance. energies, the only discrepancy being azulene (**12**). Dewar's RE (4.2 kcal/mol) is perhaps too low for azulene, which has a stability and chemical behavior more similar to benzene than to cyclic polyolefinic compounds.[26] We agree rather nicely for cyclobutadiene predicting it to be a very unstable molecule. This is in agreement with experimental evidence: cyclobutadiene was prepared[27] a few years ago only as a

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[9] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 239.

[10] E. D. Bergman in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, p 141.

[11] G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, New York, N. Y., 1969.

[12] Reference 10, p 155.

[13] J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, 177 (1956); *ibid.*, 1066 (1960).

[14] W. von E. Doering, "Theoretical Organic Chemistry," Kekulé Symposium, 1958, p 35.

[15] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); *ibid.*, **11**, 96 (1960).

[16] M. J. S. Dewar, *Chem. Ind. News*, **43**, 86 Jan 11, (1965).

[17] M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1966).

[18] A classical polyene is a polyene for which only a single classical structure (unexcited resonance structure) can be written.

[19] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 173.

[20] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965).

[21] M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969).

[22] M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc., Ser. A*, **315**, 443 (1970).

[23] Reference 19, Chapter V.

[24] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[25] E. Clar, "Polycyclic Hydrocarbons," Academic Press, London, 1964.

[26] E. Heilbronner in ref 10, p 171.

[27] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965).

highly reactive intermediate of its iron tricarbonyl complex, which cannot be isolated.[28]

Registry No.—**1**, 71-43-2; **2**, 91-20-3; **3**, 120-12-7; **4**, 85-01-8; **5**, 218-01-9; **6**, 217-59-4; **7**, 198-55-0; **8**, 191-07-1; **9**, 129-00-0; **10**, 100-42-5; **11**, 92-52-4; **12**, 275-51-4; **13**, 250-25-9; **14**, 257-24-9; **15**, 497-20-1; **16**, 539-79-7; **17**, 91-12-3; **18**, 531-45-3; **19**, 1120-53-2; **20**, 629-20-9.

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[28] NOTE ADDED IN PROOF.—After this note was submitted for publication, we noticed two important papers by B. A. Hess and L. J. Shaad [*ibid.*, **93**, 305, 2413 (1971)] describing a similar approach. We found general agreement between our results and theirs. A discussion about these two approaches is given in our paper on monocyclic conjugated molecules, submitted for publication in *Croat. Chem. Acta.*

The Photolysis of 1-Phenylcyclohexene in Methanol[1]

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The photolysis of 1-phenylcyclohexene in methanol, with or without triplet sensitizer, yields the ionic addition product, 1-methoxy-1-phenylcyclohexane.[2] This reaction was found to be susceptible to acid catalysis.[2] No other adducts or reduction products have previously been reported for this reaction. Recent reports of hydrogen atom abstraction reactions for electronically excited olefins[3] prompted us to reexamine the photolysis of 1-phenylcyclohexene in methanol.

The photolysis of degassed solutions of 1-phenylcyclohexene (I) (0.2 *M*) in methanol for 96 hr at 2537 or 3000 Å afforded four major products: phenylcyclohexane (II), 13%, 1-methoxy-1-phenylcyclohexane (III), 26%, 1-hydroxymethyl-1-phenylcyclohexane (IV), 7%, and a dimer of 1-phenylcyclohexene of undetermined structure (V), 46%. Yields are based on reacted 1-phenylcyclohexene. Quantum yield for disappearance of I at 3000 Å was 0.12. The reaction products were separated by column chromatography (Al_2O_3) and the characterized products gave ir spectra which were identical with those of authentic samples. It is noted that in previous studies[2a,b] the radiation exposures were considerably less than in the present study and that irradiation of a methanol solution of 1-phenylcyclohexene (E_T = 62 kcal/mol[4]) containing 3-methoxyacetophenone (E_T = 72.5 kcal/mol[5]) at 3500 Å gave the first three products (II, III, IV) in the above ratios and only trace amounts of dimer. 1-Phenylcyclohexene was unreactive at 3500 Å in the absence of sensitizer. A solution of 3-methoxyacetophenone in methanol and a similar solution containing 1-phenylcyclohexene were photolyzed simultaneously at 3500 Å. The quantum yield for disappearance of 3-methoxyacetophenone in the first solution was significantly lower than the quantum yield for disappearance of 1-phenylcyclohexene, thereby indicating the occurrence of triplet energy transfer rather than hydrogen atom transfer "chemical sensitization." 1,3-Cyclohexadiene (E_T = 52.5 kcal/mol[6]) quenched the photochemical formation of II, III, and IV, but not V, on irradiation at 3000 Å. These data are consistent with the following mechanism.

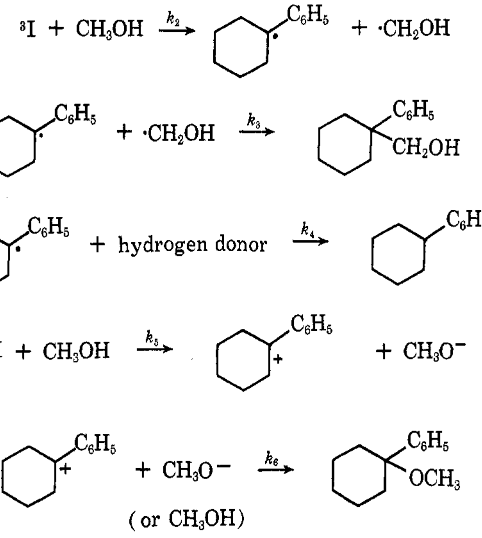
$$\mathrm{I} \xrightarrow{h\nu} {}^1\mathrm{I}$$

$${}^1\mathrm{I} + \mathrm{I} \xrightarrow{k_1} \mathrm{V}$$

$${}^1\mathrm{I} \xrightarrow{k_d} \mathrm{I}$$

$${}^1\mathrm{I} \xrightarrow{k_{ics}} {}^3\mathrm{I}$$

$${}^3\mathrm{I} \xrightarrow{k_D} \mathrm{I}$$



In the above mechanism we have assumed that phenylcyclohexane is formed *via* a hydrogen abstraction process, although there is evidence for photoreduction of some olefins.[7] We have also treated the formation of products from free radical and carbonium ion as irreversible. Although we have represented hydrogen abstraction and protonation as involving ^{3}I directly, we do not preclude prior decay of the triplet to ground state trans molecule.

Stern–Volmer quenching studies of 1-phenylcyclohexene were performed in degassed acetonitrile solu-

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[3] (a) J. Nasielski, M. Jauquet, E. Vander Donckt, and A. Van Sinov, *Tetrahedron Lett.*, 4859 (1969); (b) M. P. Servé, H. M. Rosenberg, and R. Rondeau, *Can. J. Chem.*, **47**, 4295 (1969); (c) H. M. Rosenberg and M. P. Servé, *J. Amer. Chem. Soc.*, **92**, 4746 (1970); (d) T. S. Cantrell, *Chem. Commun.*, 1633 (1970).

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