Communications TO THE EDITOR

Electrophilic Substitution of 1,3-Dichloroazulene

Sir:

The electrophilic substitution of azulene in the 1-position and disubstitution in the 3-position were shown to occur several years ago[1] and are now well-known. Further substitution of 1,3-disubstituted azulenes has, however, not been reported.

The ground state electron density calculations by Julg[2] (Fig. 1) using the self-consistent field method show the 5-position to have the next highest value after the 1- and 3-positions.[3] The localization energies[4] (Fig. 1, β-values) show essential equivalence of the 2- and 5-positions in regard to ease of electrophilic substitution.[5]

We have now achieved the acetylation of 1,3-dichloroazulene (I) by means of acetyl chloride in carbon tetrachloride with stannic chloride as the catalyst. The principal product was isolated as green needles in 16% actual (36% net) yield. The major part of these needles melted at 92–95°, with the remainder melting at 101–103°. The resolidified sample then melted at 101–103°. An analytical sample partially melted and underwent a transition at *ca.* 95°, resolidified, and then melted at 103–104°.

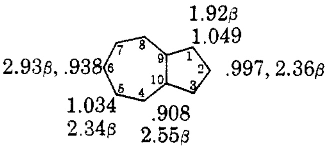
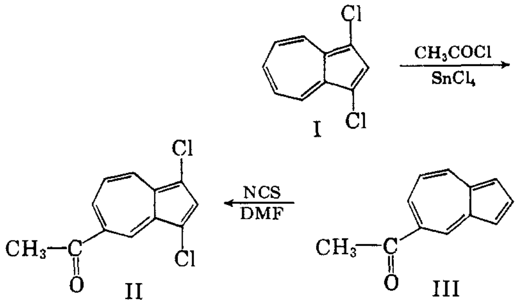


Fig. 1. Theoretical localization energies (in β) and ground state electron densities

Anal. Calcd. for $C_{12}H_8OCl_2$: C, 60.28%; H, 3.37%. Found: C, 60.55%; H, 3.29%. The infrared spectrum showed a carbonyl band at 5.97μ. A cyclohexane solution exhibited maxima in mμ (ε × 10^{-4}) in the ultraviolet at 227 (1.55), 242 (1.82), 296 (3.17), 306 (3.40), 322 (1.11), 379 (0.94), and 400 (1.62) and in the visible (ε) with a shoulder at 578 (323), shoulder at 606 (410), 627 (467), 655 (410), 664 (415), 687 (428), shoulder at 738 (183) and 769 (165).

The position (627 mμ) of the principal maximum in the visible suggested that the compound was 5-acetyl-1,3-dichloroazulene (II) on the basis of assumed additivity of the spectral shifts due to the substituents[6] (638 mμ for 1,3-dichloroazulene and −12 mμ for a 5-acetyl group[7] gives a calculated λ_{max} = 626 mμ). Proof of this structure was provided by the dichlorination of 5-acetylazulene (III)[7] in 40% yield with *N*-chlorosuccinimide in dimethylformamide. The products obtained *via* the two routes were identical (melting point; ultraviolet, visible and infrared spectra).



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[1] A. G. Anderson, Jr., J. A. Nelson, and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953). A. G. Anderson, Jr., R. Scotoni, Jr., E. J. Cowles, and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957).

[2] A. Julg, *J. Chim. phys.*, **52**, 377 (1955).

[3] These values differ from other calculated electron densities which show the 2-position to have the next highest electron density. (*cf.* E. Heilbronner, Non-Benzenoid Aromatic Compounds, D. Ginsburg, ed., Interscience Publishers, Inc., New York, 1959, p. 196).

[4] R. D. Brown, private communication to D. Peters, *J. Chem. Soc.*, 1028 (1958).

[5] These considerations do not include any possible effect of substituents in the 1,3-positions.

[6] A. G. Anderson, Jr., C. G. Fritz and R. Scotoni, Jr., *J. Am. Chem. Soc.*, **79**, 6511 (1957); E. J. Cowles, **79**, 1093 (1957); A. G. Anderson, Jr., R. Scotoni, Jr., E. J. Cowles, and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957).

[7] W. Treibs and M. Quarg, *Ann.*, **598**, 38 (1955).

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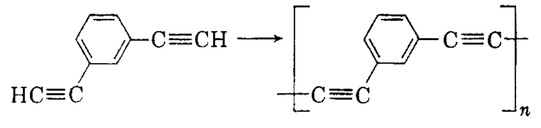
Oxidative Coupling of Acetylenes

Sir:

The oxidative coupling of acetylenes has generally been effected with air or oxygen in an ammoniacal solution of copper(I) chloride.[1] Excellent yields are generally obtained. Recently Eglinton and Galbraith[2] found that copper(II) acetate in methanolic pyridine was a superior oxidant since reactions can be carried out in homogeneous media. Sondheimer and co-workers[3] have utilized this procedure for the preparation of some unusual large ring polyacetylenes.

We have found that acetylenes can be coupled in a matter of minutes at room temperature with oxygen or air using a catalytic amount of an amine complex of a copper(I) salt in an organic solvent. Pyridine can serve as both ligand and solvent. The copper(II) carboxylates are the only copper(II) salts that are catalysts for the reaction but they are far inferior in catalytic activity to copper(I) salts.

As an example: To a 500-ml. Erlenmeyer flask there was added 250 ml. of pyridine, 2 g. of copper(I) chloride, and 50 g. (0.49 mole) of phenylacetylene. Oxygen was bubbled through the vigorously stirred reaction mixture (Fisher "Vibromixer") which was kept in a bath at 30°. A vigorous reaction ensued and the temperature rapidly rose to 40°. After 40 min. the reaction had subsided and there was isolated 42.7 g. (0.21 mole, 86% yield) of diphenyldiacetylene, colorless needles, m.p. 88° (lit., m.p. 88°).



When *m*-diethynylbenzene[4,5] is oxidized in the same manner a pale yellow polymer separates out at the end of the reaction in essentially quantitative yield. *Anal.* for $C_{10}H_4$: C, 96.8; H, 3.2. Found C, 96.4; H, 3.5. The polymer is soluble in solvents such as chlorobenzene and nitrobenzene above 100°. Evaporation of a nitrobenzene solution at 170° yields transparent, flexible films. Infrared analysis of end groups ($\equiv$CH stretching, 3290 cm.$^{-1}$) indicates a molecular weight of at least 7000[6] and intrinsic viscosities (nitrobenzene, 150°) as high as 0.25 decil./g.[6] have been obtained. This material appears to be quite stable at room temperature. When rapidly heated *in vacuo* it abruptly decomposes at about 180°, evolving hydrogen and a small amount of methane[6] and leaving a residue of carbon. When ignited at room temperature in air an explosive reaction takes place; however, the net result is the loss of most of the hydrogen and some carbon, presumably as carbon dioxide, for a total weight loss of only 5–6%.

Oxidation of *p*-diethynylbenzene[5] gives a bright yellow product that is completely insoluble in all solvents we have tried and decomposes rapidly at about 100°.

Aliphatic ethynyl compounds are also oxidized with catalysts of this type. Further work will be reported in the near future.

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[1] R. A. Raphael, *Acetylene Compounds in Organic Synthesis*, Academic Press Inc., New York, 1955, p. 127.

[2] G. Eglinton and A. R. Galbraith, *Chem. & Ind.* (*London*), 737 (1956).

[3] F. Sondheimer, R. Wolovsky, and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 755 (1960) and previous papers.

[4] R. Deluchat, *Ann. chim.* [11], **1**, 181 (1934).

[5] A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).

[6] We are indebted to Dr. P. D. Zemany for mass spectrometric analyses, to Drs. R. S. McDonald and A. E. Newkirk for infrared analyses, and to Mr. J. W. Eustance for determination of intrinsic viscosities.

Volatile Methyl Ketone Formed in Rubber Oxidation

Sir:

Tobolsky and Mercurio[1] have suggested that the volatile methyl ketone produced in high yield during the oxidation of rubber is 2,5-hexanedione rather than levulinaldehyde; no experimental support for this suggestion was offered.

The original identification of levulinaldehyde as an oxidation product was made by Whitby,[2] who gave no details in his report. We wish to report the following observations in confirmation of Whitby's identification. Treatment of the liquid condensed[3] from the reaction of 200 ml. of oxygen and 2-3 g. of rubber at 120° and 1 atm. with 2,4-dinitrophenylhydrazine reagent[4] yields a crude bisdinitrophenylhydrazone whose X-ray diffraction pattern is indistinguishable from that of authentic levulinaldehyde bis-2,4-dinitrophenylhydrazone,[5]

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[3] E. M. Bevilacqua, *J. Am. Chem. Soc.*, **79**, 2915 (1957); **80**, 5364 (1958).

[4] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, 4 ed., 1956, p. 111.

[5] C. L. Wilson, *J. Am. Chem. Soc.*, **70**, 1313 (1958).