

energy maxima separating the two rotamers are computed to have energies of less than 5 kcal/mol higher than those of the stable forms. Molecules possessing the CH_2F -moiety are seen to possess stable *trans* and *cis* forms, whereas those substances having a CH_2Cl -group have stable *trans* and *gauche* rotamers.

Unfortunately, incomplete experimental data are available to check the calculations performed on the CH_2Y -CXO compounds. Moreover, the existing experimental information has been derived from "bottoms" of the potential wells, and virtually no complete potential curve has been determined experimentally. The most exhaustive study available appears to be one performed by Saegebarth and Wilson⁴ on CH_2F -CFO as mentioned in the introduction. As can be seen from Table 2 there is very good agreement between their results and the present computations regarding the relative stability of the two forms. Insufficient information was available to draw a complete potential function for this molecule, but the one suggested by Saegebarth and Wilson⁴ closely resembles the CNDO/2 result of Table 2. The dipole moments of the two forms⁴ are 2.67 ± 0.05 D for *trans* and 2.05 ± 0.06 D for *cis* which compare well to the computed values of 2.68 D and 1.79 D, respectively.

The existence of two forms of CH_2Cl -CHO has now been experimentally established.¹⁰ This is in agreement with the present findings.

For CH_2F -CHO, CH_2F -CClO, and CH_2Cl -CFO no experimental data have been found in the literature. By comparing the calculated potential curves of these molecules to those for which experimental information is available, a few interesting features are observed. *E.g.*, the CH_2F -CHO potential function resembles that of CH_2F -CFO, with the difference that the *cis* form is relatively more stable for the former molecule. This seems quite plausible for steric reasons because there is probably a slight repulsion⁴ between the fluorine atoms in *cis* CH_2F -CFO, whereas steric conditions are probably more favourable in *cis* CH_2F -CHO. For CH_2F -CClO and CH_2Cl -CFO virtually no experimental data exist to check the computational results.

Acknowledgement. The author is grateful to cand. real. Harald H. Jensen for his help and encouragement. Financial support from the

Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

1. Kilb, R. W., Lin, C. C. and Wilson, Jr., E. B. *J. Chem. Phys.* **26** (1957) 1695.
2. Pierce, L. and Krisher, L. C. *J. Chem. Phys.* **31** (1959) 875.
3. Sinnott, K. M. *J. Chem. Phys.* **34** (1961) 851.
4. Saegebarth, E. and Wilson, Jr., E. B. *J. Chem. Phys.* **46** (1967) 3088.
5. Nakagawa, J., Ichishima, J., Kuratani, K., Miyazawa, T., Shimanouchi, T. and Mizushima, S. *J. Chem. Phys.* **20** (1952) 1720.
6. Morino, Y., Kuchitsu, K. and Sugiura, M. *J. Chem. Soc. Japan* **75** (1954) 721.
7. Davidson, R. B. and Allen, L. C. *J. Chem. Phys.* **54** (1971) 2828.
8. Pople, J. A. and Segal, G. A. *J. Chem. Phys.* **43** (1965) S129.
9. Pople, J. A. and Beveridge, D. L. *Approximate Molecular Orbital Theory*, McGraw, New York 1970.
10. Ford, R. G. *Symposium on Molecular Structure and Spectroscopy*, Ohio 1971, F12.
11. Zahn, C. T. *Phys. Z.* **33** (1932) 686.

Received October 23, 1972.

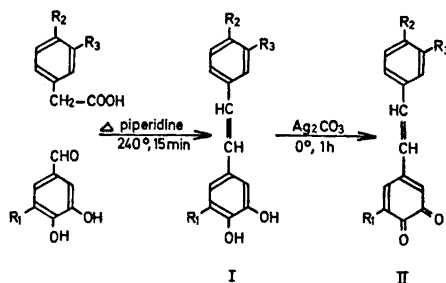
Synthesis of 3,4-Stilbenequinones

JOSEF GIERER and
AUGUSTINE E. OPARA

*Chemistry Department, Swedish Forest
Products Research Laboratory, Box 5604,
S-114 86 Stockholm, Sweden*

3,4-Stilbenequinoid structures are of considerable interest as possible chromophoric constituents of sulfite and sulfate pulps.¹ Apparently, the instability of this particular type of chromophoric system has hitherto handicapped the preparation of representative models. Our efforts to synthesize models of this type employing familiar routes such as oxidation with potassium nitrosodisulfonate (Fremy-salt),²

Table 1.



Substituents	Yield of I	m.p.	Yield of II	m.p.
(a) $R_1 = R_2 = R_3 = H$	10	167°	95	210°
(b) $R_1 = H; R_2 = R_3 = OCH_3$	8	148°	90	165°
(c) $R_1 = OCH_3; R_2 = R_3 = H$	13	95°	90	170°
(d) $R_1 = R_2 = R_3 = OCH_3$	16	121°	89	147°

sodium metaperiodate,³ and argentic oxide⁴ have been unsuccessful.

We now wish to report a simple two-step synthesis for preparing 3,4-stilbenequinones. The procedure involves the synthesis of catechol-type stilbenes (3,4-stilbenediols, I a–d) which is accomplished by condensing equimolar amounts of the appropriate phenylacetic acid and 3,4-dihydroxybenzaldehyde in the presence of a small amount of piperidine (240–260°; 15 min) according to the method described for 3-methoxy-4-stilbenol.⁵ Chromatography of the resulting mixture on silica gel gives the corresponding 3,4-stilbenediol (I a–d, see Table 1).

The 3,4-stilbenediols are then oxidized to the *o*-quinones with silver carbonate on Celite.⁶ The following description exemplifies the oxidation procedure: 3,4-Stilbenediol (200 mg) in benzene (100 ml) was stirred with silver carbonate on Celite (6.0 g) at 0° for 1 h. After separation of the Celite by filtration, the orange solution was evaporated under reduced pressure at 40° to give 3,4-stilbenequinone (IIa) as dark prisms, m.p. 209–210° (95% yield). Quinones II (b–d) (see Table 1) were similarly prepared. The quinones were highly pure and needed no further purification.

The oxidation with silver carbonate-Celite of catechuic structures to the *o*-

quinones was also successfully applied to catechols carrying a conjugated carbonyl group in a *para*-position. Thus, 3,4-dihydroxy-5-methoxy-acetophenone gave the corresponding methoxy-*ortho*-quinone in 65% yield (m.p. 160°).

The identity of the quinones has been confirmed by IR, UV, NMR, and mass spectra, as well as by elemental analyses of the quinones and their phenazines. The quinones exhibit strong absorption near 390 and 500 nm indicative of *o*-quinoid chromophores.⁷

- Gierer, J. *Svensk Papperstid.* **18** (1970) 571.
- Zimmer, H., Lankin, D. C. and Horgan, S. *W. Chem. Rev.* **71** (1970) 229.
- Adler, E. and Magnusson, R. *Acta Chem. Scand.* **13** (1959) 505.
- Snyder, C. D. and Rapoport, H. *J. Am. Chem. Soc.* **94** (1972) 227.
- Walczak, E. and Wieniawski, W. *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **12** (1964) 823.
- Balough, V., Fétizon, M. and Golfier, M. *J. Org. Chem.* **36** (1972) 1339.
- Teuber, H. J. and Staiger, G. *Chem. Ber.* **88** (1955) 802.

Received October 19, 1972.