Diels–Alder Dimerization of 2-Arylmaleimides. *X*-Ray Crystal Structure of the Dimer of 2-*p*-Tolylmaleimide

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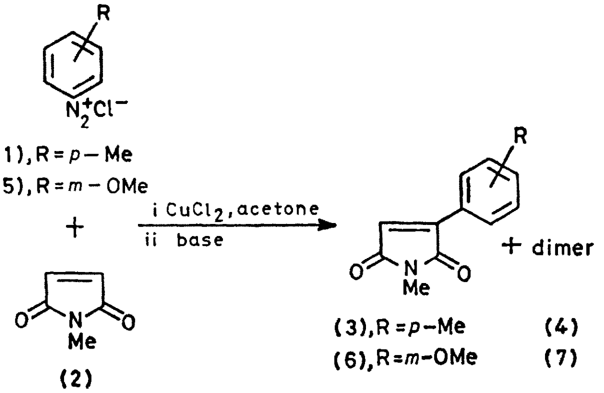
Summary Dimers (**4**) and (**7**) were obtained during the course of the Meerwein arylation reaction; a Diels–Alder reaction is proposed for the mechanism of the dimerization, and the *X*-ray structure of (**4**) is reported.

IN connection with another problem,[1] we required a variety of 2-arylmaleimides. These are conveniently prepared by the copper(II) catalysed coupling of aryl diazonium cations with maleimides (Meerwein reaction).[2] The coupling reaction is carried out in aqueous acetone at pH 3, to give the 3-chloro-2-aryl-succinimides, and probably involves aryldiazenatocuprate complexes.[3] The chlorosuccinimide intermediates are then heated on a steam-bath with an excess of 2,6-lutidine to complete the sequence.

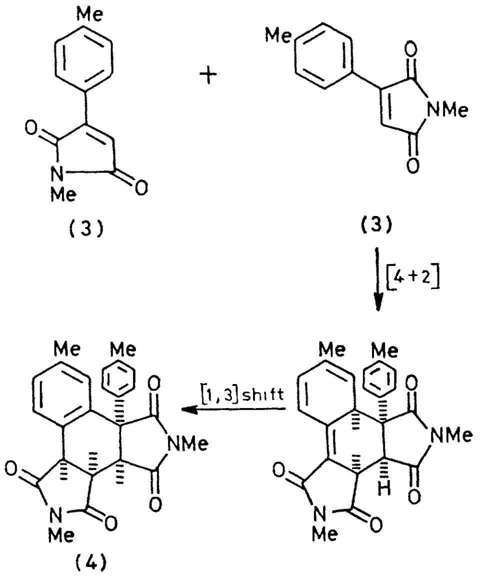


(1), R = *p*-Me
(5), R = *m*-OMe

(3), R = *p*-Me (4)
(6), R = *m*-OMe (7)

(2)

When the diazonium salts (**1**) and (**5**), containing electron releasing substituents, were condensed with (**2**), the major products isolated were high melting dimers (**4**)† (m.p. 330—332 °C) and (**7**)† (m.p. 281—283 °C) as well as lesser amounts of (**3**)† (m.p. 118—122 °C)[4] and (**6**)† (m.p. 150—151 °C).[1] The structure of (**4**) was rigorously established by single crystal *X*-ray diffraction. Many by-products have been reported from the Meerwein arylation[2] but, to our knowledge, this dimerization is new.



(3) (3)

(4)

Crystal data (**4**), $C_{24}H_{22}N_2O_4$, $M = 402{\cdot}4$, monoclinic, $a = 15{\cdot}120(7)$, $b = 17{\cdot}010(11)$, $c = 8{\cdot}272(4)$ Å, $\beta = 104{\cdot}14(5)^\circ$, $Z = 4$, $D_c = 1{\cdot}296$ g cm^{-3}, $D_m = 1{\cdot}29$ g cm^{-3}, space group $P2_1/c$.

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† The combustion analysis, i.r., ^{1}H- and ^{13}C-n.m.r., mass, and u.v. spectra of this compound were in agreement with the assigned structure.

Reflections in the range $6° \leqslant 2\theta \leqslant 120°$ were recorded with Cu-K_{α} radiation; 2015 reflections were considered observed by the criterion $I > 2{\cdot}0\,\sigma(I)$. The structure was solved by direct methods[5] and refined with anisotropic non-hydrogen atoms to a final R-factor of 9·6%.‡

The dimer (**4**) appears to result from an *endo* oriented [4 + 2] cycloaddition followed by a [1,3] suprafacial hydrogen shift. A carefully purified sample of authentic (**3**),[1] isolated from the Meerwein reaction, slowly dimerized to (**4**) in hot 2,6-lutidine solution (100 °C, 0·20 M, 45 h, 94% yield) but was recovered unchanged from refluxing 1,2-dichloroethane (b.p. 83 °C, 0·18 M, 24 h).

The Diels–Alder addition of styrenes as the diene component is well known[6] but it is claimed that an alkoxy group in the *para* position is a requisite for reaction. The suprafacial [1,3]sigmatropic rearrangement leading to (**4**) is thermally forbidden[7] so the basic solvent lutidine must be required to catalyse the hydrogen shift and thus drive the two-step reaction to the observed dimer.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] W. J. Fanshawe, J. W. Epstein, L.S. Crawley, C. M.Hofmann, and S. R. Safir, U.S.P. **4,131,611** (1978).
[2] C. S. Rondestvedt, *Org. React.*, 1976, **24**, 225.
[3] D. Sutton, *Chem. Soc. Rev.*, 1975, **4**, 443.
[4] M. Augustin, M. Koehler, G. Erfurt, S. Mueller, and W. Kochmann, G. D. R. P. **103,136** (1974).
[5] G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, 1970, B, **26**, 274; 1971, **A27**, 368.
[6] B. J. F. Hudson and R. Robinson, *J. Chem. Soc.*, 1941, 715.
[7] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, 1970, p. 120.