

Diels–Alder Reaction of Quinones generated *in situ* by Electrochemical Oxidation in Lithium Perchlorate–Nitromethane

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Oxidative formation and Diels–Alder reaction of several *p*- and *o*-quinones are carried out *in situ* with dienes in an electrochemical reaction system of lithium perchlorate–nitromethane.

Quinones are widely employed as dienophiles in Diels–Alder reactions. Unstable quinones possessing electron-withdrawing groups are, however, difficult to isolate and decompose readily under the usual conditions of Lewis acid catalysis. Recently, lithium perchlorate in diethyl ether has been reported to accelerate Diels–Alder reactions,¹ and the role of Li⁺ and perchlorates has been discussed extensively.² In the present study, we accomplished one-pot electrochemical formation of various *p*- and *o*-quinones, followed by Diels–Alder reaction with dienes in excellent yields by using a lithium perchlorate–nitromethane system.

In a preliminary study, *p*-benzoquinone, dissolved in a 1.0 mol dm⁻³ solution of lithium perchlorate in nitromethane was treated with 1.0 equiv. of α -terpinene **2** at ambient temperature. After 16 h, the completed reaction gave **3** in nearly quantitative yield, whereas the reaction in 1.0 mol dm⁻³ lithium perchlorate in acetonitrile, diethyl ether or methanol gave **3** in lower yield (14.3, 29.4 and 0%, respectively). The current of the anodic oxidation of **1** in lithium perchlorate–nitromethane was soon lowered by the adsorption of compounds on the carbon electrode; however, its oxidation and

subsequent cycloaddition with diene **2** was found to proceed successfully in the presence of a small amount of acetic acid in 1.0 mol dm⁻³ lithium perchlorate–nitromethane. On the other hand, the electrochemical reaction was not successful in acetonitrile, diethyl ether or methanol, even in the presence of acetic acid or in varied concentrations of lithium perchlorate. Accordingly, the following reactions were performed in lithium perchlorate–nitromethane containing acetic acid.

Table 1 shows the results of electrochemical oxidation of hydroquinone derivatives and *in situ* Diels–Alder reaction *via* stable quinones. The reaction gave *endo* adducts mainly, and in the absence of dienes, the intermediate quinones could be isolated. In the presence of a small amount of water, *p*-methoxyphenol derivative **15** was oxidized *via* hydrolysis of *p*-methoxy group to give cycloadducts **13** and **14**. Further-

Table 2 Electrochemical oxidation of hydroquinones and catechols, and Diels–Alder reactions of the corresponding *p*- and *o*-quinones with dienes

Table 1 Electrochemical oxidation of hydroquinones and Diels–Alder reactions of the corresponding quinones with dienes

Hydroquinone	Diene	Product	Yield (%)
			97
			96
			82 (1:1)
			96 (1:1)
			93 (1:1)
			90 (1:1)

Hydroquinone or catechol	Diene	Product	Yield (%)
			97
			90
			98
			98
			91
			98
			94
			92 (1:1)
			97

more, cycloadducts of unstable *p*- and *o*-quinones with dienes were obtained in high yield† (Table 2). Selectivity for *ortho*- or *para*-like cycloaddition was observed between the outer-ring carbonyl groups of **16**, **18** or **20** and methyl groups of **4** or **24**. In the reaction of catechol derivatives, regioselectivity was also found except for that of **26** and **4** which gave both *para*- and *meta*-like adducts (**28** and **29**). In addition, only **32** was isolated as the α -dione form which may be the result of the repulsion between the C4-methyl and C5-acetyl groups to fix the *cis* ring junction.

In conclusion, the procedure employing electrochemical oxidation in 1.0 mol dm⁻³ lithium perchlorate–nitromethane is applicable to form a variety of quinones. In these cases involving unstable quinones, Diels–Alder reactions proceeded smoothly with dienes to give cycloadducts including those which are difficult to obtain in high yield by other methods.

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Footnote

† *General procedure*: Anodic oxidation of **26** (91 mg, 0.5 mmol) in 10 ml of MeNO₂ containing dry LiClO₄ (500 mg) as supporting electrolyte, AcOH (50 mg), and 2,3-dimethylbutadiene **21** (49 mg, 0.6 mmol) was carried out at a constant potential (1200 mV vs. saturated calomel electrode), using a glassy carbon plate (60 × 20 × 3 mm) as anode and a platinum plate (10 × 10 mm) as a cathode, respectively, without separating the two electrodes under Ar. The reaction was quenched after 16 h to afford cycloadduct **27** in 98% isolated yield.

References

- 1 P. A. Grieco, J. J. Nunes and M. D. Gaul, *J. Am. Chem. Soc.*, 1990, **112**, 4595; M. A. Forman and W. P. Dailey, *J. Am. Chem. Soc.*, 1991, **113**, 2761.
- 2 H. Waldman, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1306; D. A. Smith and K. N. Houk, *Tetrahedron Lett.*, 1991, **32**, 1549; G. Desimoni, G. Faita, P. P. Righetti and G. Tacconi, *Tetrahedron*, 1991, **47**, 8399; R. M. Pagni, G. W. Kabalka, S. Bains, M. Plesco, J. Wilson and J. Bartmess, *J. Org. Chem.*, 1993, **58**, 3130; S. Fukuzumi and T. Okamoto, *J. Am. Chem. Soc.*, 1993, **115**, 11600.