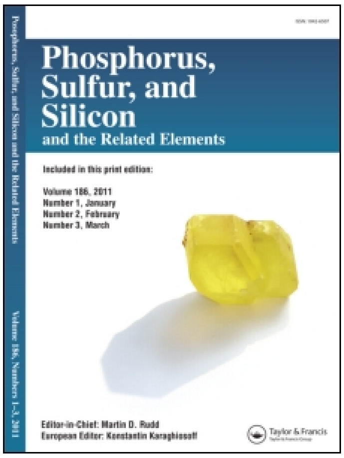

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THE MARKOVNIKOV-ANTIMARKOVNIKOV ADDITION OF *m*-THIOCRESOL AND *p*-NITROTHIOPHENOL TO INDENE

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The addition of *m*-thiocresol and *p*-nitrothiophenol to indene has been studied under a variety of acidic conditions. The reaction of indene and *m*-thiocresol gave both Markovnikov and anti-Markovnikov adducts, in 58% and 42% yields, respectively. Surprisingly, in the reaction of *p*-nitrothiophenol and indene only the anti-Markovnikov adduct was formed. No adduct was obtained when this last reaction was run in the absence of an acid catalyst, whereas the anti-Markovnikov adduct was the only product formed in the case of *m*-thiocresol.

INTRODUCTION

It is surprising that not even chromatographic evidence was found in the course of our many thiol-olefin cooxidation (TOCO) studies that suggests the formation of the Markovnikov (M) adducts from various thiols and indene or styrenes even though the anti-Markovnikov (anti-*M*) adducts can indeed be formed as by-products of the TOCO reaction.[1] Contrary to the commonly held impression, thiols and olefins give M adducts only reluctantly although attempts to catalyse the reaction by means of sulfur,[2] acids[3] and under Friedel-Crafts[4] or basic[5] conditions are reported. For this reason we have subjected a typical aromatic thiol, namely *m*-thiocresol (**1**) and the strongly acidic aromatic thiol, *p*-nitrothiophenol (**2**) to a variety of acidic conditions in the presence of indene (**3**) in order to elucidate the conditions for the formation of the M adduct.

RESULTS AND DISCUSSION

The reaction of (**1**) and (**3**) carried out over a period of 5 days in isooctane and in the presence of *p*-toluenesulfonic acid gave both the M(**4**) and anti-M(**5**) products in

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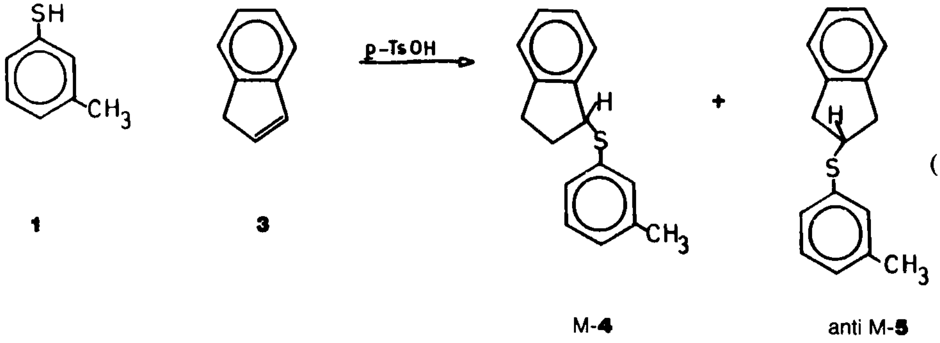


(1)

58% and 42% yields, respectively (eq. 1). On the other hand, an analogous reaction in a mixture of dioxane-deuterochloroform gave (4) in a 22% yield over a period of 8 days. The last mentioned experimental conditions were suitable to follow the reaction by means of NMR and it is noted that the distribution of products (4) and (5) varies dramatically with time. Thus, although (5) is formed rapidly at the beginning and is the only adduct detected during the first 24 hours, the slow formation of (4) eventually produces 3.3 : 1, 2.5 : 1 and 2 : 1 mixtures of (5) and (4) after 8, 16 and 31 days, respectively. A more precise estimate of the relative ease of the formation of (4) and (5) was obtained when a solvent mixture of acetic acid and chloroform was used in the presence of some cyclohexane which served as an internal NMR standard (Figure 1). These results seem to indicate that traces of oxygen were responsible for the initial rapid formation of (5) whereas the acid-catalyzed formation of (4) was extremely slow by comparison. The formation of (5) came to a halt when the traces of oxygen were consumed in the typical cooxidation reaction.[1]

Considering the acid-catalyzed formation of **4**, it seemed possible that the rather acidic (**2**) might undergo an autocatalyzed formation of the Markovnikov product. This, however, was not the case. In the absence of an external acid catalyst, (**2**) and (**3**) gave only some di-*p*-nitrophenyl disulfide and the bulk of the reactants was recovered. Thus, although many aromatic thiols exposed to traces of oxygen in the presence of (**3**) produce the anti-M adducts,[6] thiol (**2**) gives only the corresponding disulfide. The reaction of (**2**) and (**3**) was also carried out over a period of 4 days in the presence of acetic, trifluoroacetic and *p*-toluenesulfonic acids. Surprisingly enough under these conditions, the product turned out to be the anti-M adduct (**6**) (eq. 2). These reactions of (**2**) and (**3**) were also monitored by means of the convenient NMR technique. The effect of the different acidic catalysts on the formation of (**6**), shown in Figure 2, clearly indicates that the formation of (**6**) although slow, is favored by the stronger acids.

The "normal" formation of the M product (**4**) under relatively weakly acidic conditions in the case of (**1**) needs explanation since (**2**) fails to give an adduct under similar conditions and requires strong acid for addition to **3** but then gives the "abnormal" anti-M adduct. A possible rationale for the dramatic difference in

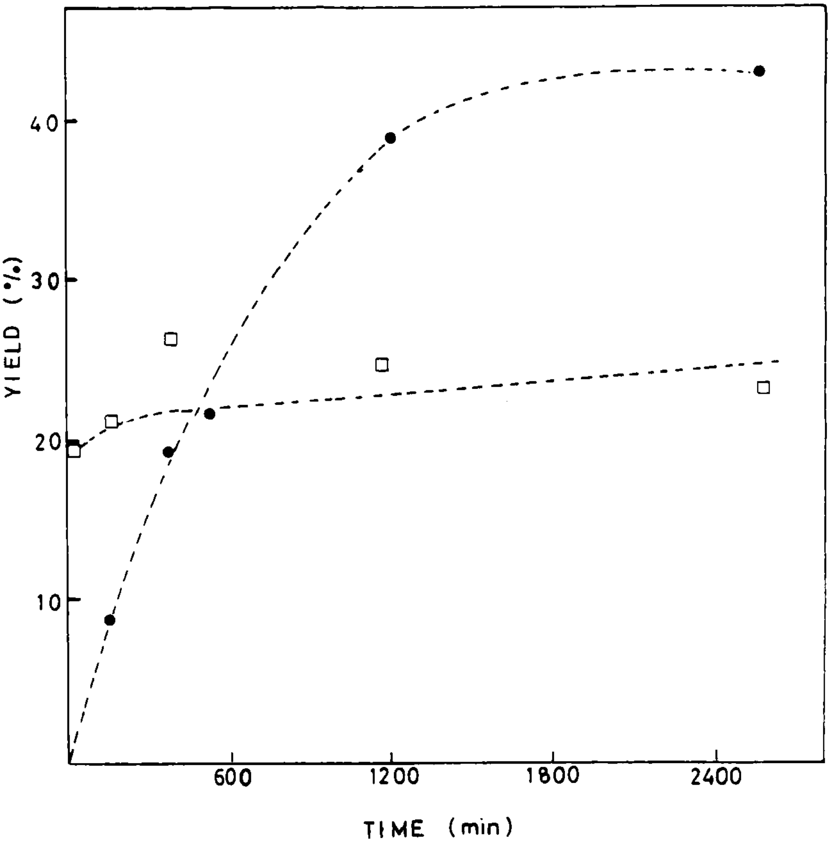
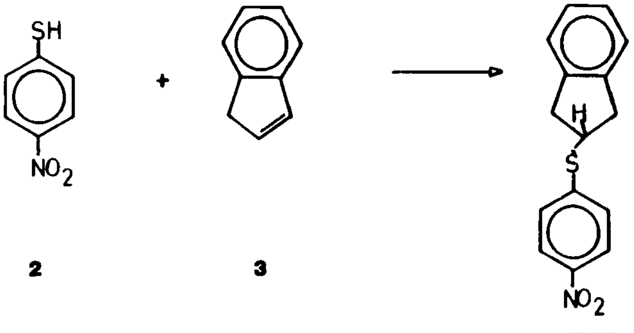


FIGURE 1 The yields of **4** and **5** in the reaction of *m*-thiocresol and indene. Solvent System: acetic acid-chloroform (2 : 1 v/v). (see Experimental). (□) 1-Indanyl *m*-methylphenyl sulfide (**4**); (●) 2-Indanyl *m*-methylphenyl sulfide (**5**).



2 **3**

anti M-**6**

(2)

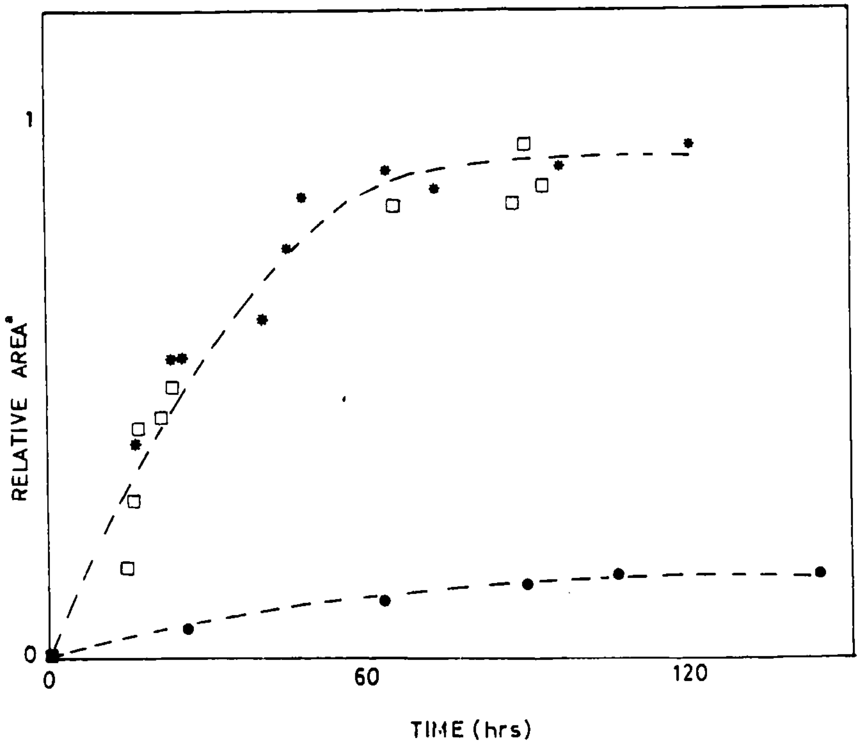
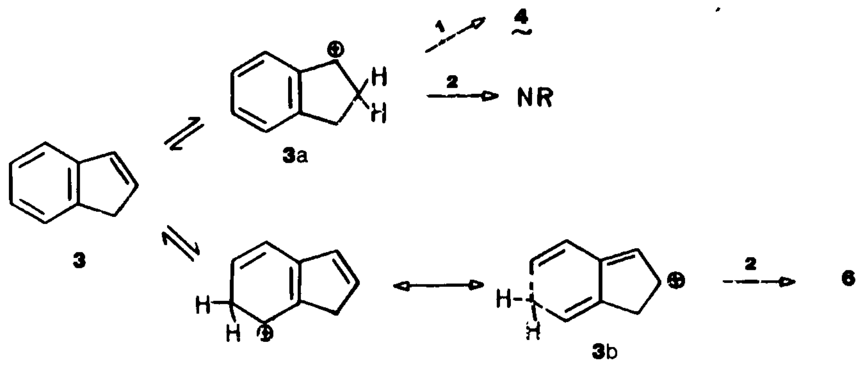


FIGURE 2 The effect of different acidic catalysts on the formation of **6** (see Experimental). (*) Trifluoroacetic acid[b]; (□) *p*-Toluenesulfonic acid[b]; (●) Acetic acid.

[a] The area of two methylene protons in 2-indanyl *p*-nitrophenyl sulfide (**6**) relative to cyclohexane.

[b] The plateau is reached when almost no signal for indene is observed.



SCHEME 1

the behavior of (**1**) and (**2**) depends on the likely equilibria in the formation of the protonated intermediates derived from (**3**) (Scheme 1). It can be assumed that acids are more likely to protonate the exocyclic double bond of (**3**) than the highly resonance-stabilized benzene moiety. Protonation may give carbocation (**3a**), which then may react with (**1**) to give (**4**), while (**2**), it would appear, either fails to react or reacts reversibly. Protonation of (**3**) on the benzene is apparently required to provoke irreversible reaction with (**2**). An examination of carbocations derived from (**3**) reveals (**3b**) as a possible intermediate that can lead to the formation of (**6**).

Further work is in progress to elucidate this unexpected formation of anti-M adducts under strongly acidic conditions.

EXPERIMENTAL PART

Materials. *m*-Thiocresol and indene (Aldrich) were purified by distillation under vacuum. *p*-Nitrothiophenol was used without purification. 1-Indanyl chloride was prepared from indene and hydrogen chloride as described elsewhere.[7]

All the compounds reported here gave satisfactory C, H, S and N microanalytical results.

1-Indanyl m-Methylphenyl Sulfide. This compound was synthesized in 63% yield by the reaction of 1-indanyl chloride with sodium thiophenolate using a general procedure described in the literature.[7] The compound was purified by vacuum distillation: bp 131–135°C (1.5 torr). ^{1}HNMR $\delta(CDCl_3)$; 2.2 (s, 3 H), 2.8 (m, 4 H), 4.59 (t, 1 H, $J = 5$ Hz), 7.08 (m, 8 H).

2-Indanyl p-Nitrophenyl Sulfide. p-Nitrothiophenol (0.69 g, 4.5 mmol), indene (0.5 g, 4.5 mmol) and trifluoroacetic acid (0.17 g, 1.5 mmol) in 5.5 ml $CHCl_3$ were stirred at room temperature. After 4 days the reaction mixture was washed with a dilute sodium hydroxide solution and water, and the organic phase was then dried over anhydrous $MgSO_4$. The crude product was purified by means of a silica gel column using hexane as eluent (50% yield) mp 107°C, R_f 0.74 (TLC silica gel, eluent: ethyl acetate 10%, hexane 90%). ^{1}HNMR $\delta(CDCl_3)$: 3.0 (dd, 2 H), 3.53 (dd, 2 H), 4.23 (m, 1 H), 7.33 (m, 6 H), 8.86 (m, 2 H). MS (m/e 60 ev): 271 [M^+] (57), 117 (base peak), 116 (95), 115 (77.2), 91 (29.1), 65 (9.4).[8]

A similar result was obtained with *p*-toluenesulfonic acid

Reaction of p-Nitrothiophenol and Indene in the Absence of Catalysts. From a solution of *p*-nitrothiophenol (3.1 g, 20 mmol) and indene (2.3 g, 20 mmol) in 60 cc of ethyl acetate there were separated after 9 days at 30°C, 0.3 g of disulfide mp 178–179°C (9.8% of starting material),[9] and 83.8% of the original thiol.

m-Thiocresol-Indene in the Absence of Catalysts. Indene (2.32 g, 20 mmol) and *m*-thiocresol (2.48 g, 20 mmol) in ca. 60 ml of cyclohexane were allowed to react during 9 days at room temperature in a nitrogen atmosphere. The reaction was quenched by using 10% sodium hydroxide solution. Recrystallization from 95% EtOH: mp 42–43°C. ^{1}HNMR $\delta(CDCl_3)$: 2.42 (s, 3 H), 3.15 (m, 4 H), 4.01 (m, 1 H), 7.12 (s, 4 H), 7.45 (m, 2 H), 7.73 (m, 2 H). The anti-Markovnikov (38% yield) was the only product formed. This sulfide was identical to that described previously.[6]

m-Thiocresol-Indene in Presence of p-Toluenesulfonic Acid. Indene (2.32 g, 20 mmol) and *m*-thiocresol (2.48 g, 20 mmol) were refluxed in ca. 60 ml of isooctane in the presence of *p*-toluenesulfonic acid (0.04 g, 0.2 mmol). After 5 days the reaction was washed with a saturated solution of sodium bicarbonate followed by dilute sodium hydroxide and water. The mixture of products was separated by means of a silica gel column using petroleum ether and chloroform as eluents. The addition products consisted of 42% of 2-indanyl *m*-methylphenyl sulfide and 58% of 1-indanyl *m*-methylphenyl sulfide. These two adducts were identical to those described above.

NMR Study of Acid-Catalyzed Addition of Thiophenols to Indene. The reactions were carried out in a NMR tubes and monitored by means ^{1}HNMR by following the appearance of the signal of methylene group of **6** and the methyl group in the cases of **4** and **5**.

m-Thiocresol-Indene System. a) Dioxane-$CDCl_3$ solvent mixture. *m*-Thicresol (0.43 g, 3.4 mmol) and indene (0.4 g, 3.4 mmol) were added, to *p*-toluenesulfonic acid (0.02 g, 0.1 mmol) dissolved in 0.1 cc of dioxane). A gelatinous precipitate was formed when the indene was added but a clear solution was obtained upon addition of 0.1 cc of $CDCl_3$.

b) Acetic acid-$CDCl_3$ solvent mixture. *m*-Thiocresol (0.14 g, 1.15 mmol) in 0.1 ml of $CDCl_3$, indene (0.13 g, 1.15 mmol) in 0.2 ml of acetic acid, and *p*-toluenesulfonic acid (0.04 g, 0.23 mmol) were allowed to react at 32°C. Cyclohexane was used as internal standard.

c) Control Experiment. In order to test the possibility of isomerization of 1- and 2-indanyl *m*-methylphenyl sulfide, solutions of each sulfide (1.15 mmol) in a mixture of 0.1 ml of $CDCl_3$, 0.2 ml of acetic acid and *p*-toluenesulfonic acid (0.04 g, 0.23 mmol) were examined at 32°C. No changes in the NMR spectra were observed over a period of 15 days.

p-Nitrothiophenol-Indene system. *p*-Nitrothiophenol (0.16 g, 1.03 mmol) and indene (0.12 g, 1.03 mmol) were dissolved in 0.7 ml of $CDCl_3$ that contained 0.15 mmol of different catalysts (trifluoroacetic acid, *p*-toluenesulfonic acid and acetic acid). The results are summarized in Fig. 2.

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