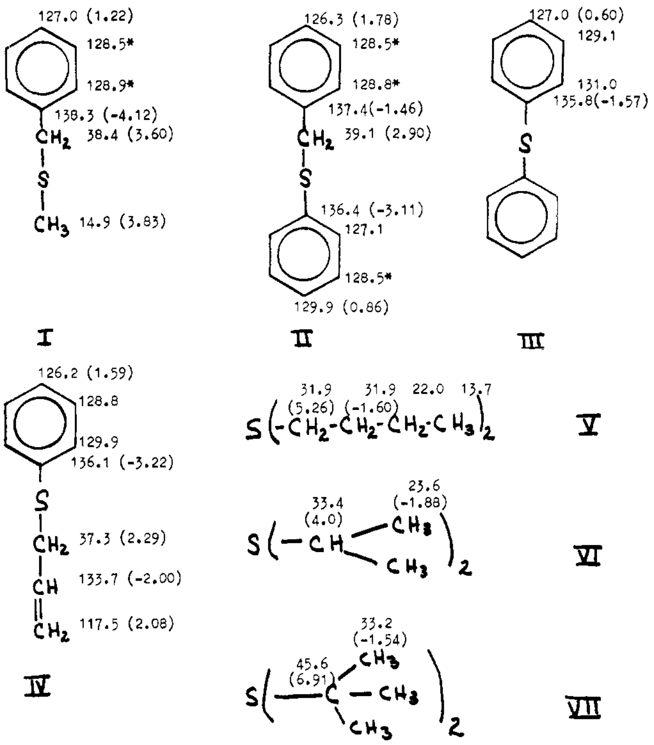

Figure 2. Carbon-13 chemical shifts and iodine-induced chemical shifts (slope of the δ_{obsd} vs. molar concentration plot) for the sulfides. *Assignments may be reversed.

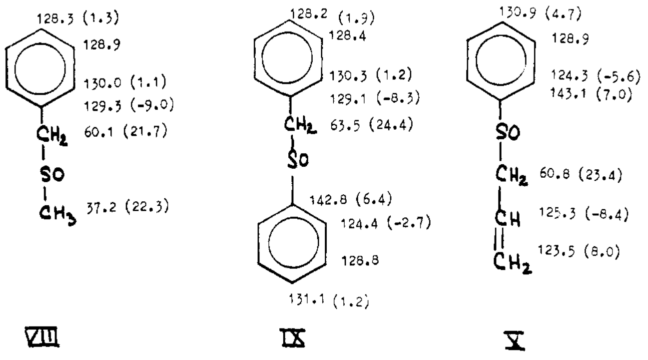

Figure 3. Carbon-13 chemical shifts and substituent chemical shifts (where negative values indicate upfield shifts) for the sulfoxides as compared to the sulfides.

An upfield shift would indicate an increase of electron density as compared to the parent sulfide. Except for compound IV, the only iodine-induced shift of any magnitude occurs for the para-aromatic ring carbons which invariably are shifted to lower field.

The net result of the iodine-induced shifts illustrated for compound II is shown below. The type of electronic interaction found in the sulfide–iodine complex is best explained by a π-bond polarization mechansim.[11] Strong evidence supporting the π-bond polarization of these systems can be found in the induced shifts for the olefinic carbons in XI. Clearly, both of these carbon resonances are affected to the same degree but in opposite directions, as predicted by the π-bond polarization mechanism. Further support for the π-bond polarization mechanism can be seen in the substituent shifts of the sulfoxides VIII, IX, and X; see Figure 3.[12]

Experimental Section

All of the sulfides were commercially available and are estimated by VPC to be greater than 99% pure. The sulfoxides were obtained from C. G. Venier, Texas Christian University, and were used as received. The iodine-induced shifts were obtained by an incremental addition of iodine to a 0.5 M solution of the sulfide in deuteriochloroform contained in a 10-mm o.d. NMR tube.

The carbon-13 magnetic resonance spectra were obtained in the Fourier transform mode on a JEOL FX-60 spectrometer system equipped with a 24K memory Texas Instruments computer. The spectra were obtained at an observing frequency of 15.03 MHz. General NMR spectral parameters were: internal lock to the deuterium containing solvent; a spectral width of 2500 Hz; a pulse width of 4 μm corresponding to a 36° pulse angle; and a pulse repetition time of 2.1 s. All shifts are estimated to be accurate to ±0.05 ppm and are referenced to internal Me_4Si.

Acknowledgments. The financial support of this work by the Robert A. Welch Foundation is gratefully acknowledged. The author also thanks the National Science Foundation and the National Institutes of Health for their grants to Professor P. D. Bartlett which enabled the purchase of the JEOL FX-60 spectrometer system. In addition, the author thanks Professor P. D. Bartlett for the opportunity to engage this project and Professor C. G. Venier for the sulfoxides used and for helpful discussions.

Registry No.—I, 766-92-7; II, 831-91-4; III, 139-66-2; IV, 5296-64-0; V, 544-40-1; VI, 625-80-9; VII, 107-47-1; VIII, 824-86-2; IX, 833-82-9; X, 19093-37-9; iodine, 7553-56-2.

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(9) The "limiting shift" obtained by this method is dependent upon the absolute concentration of the sulfide. Experimentally this can be resolved by performing the experiment keeping the iodine concentration constant and varying the sulfide concentration. Since an accurate limiting shift or equilibrium constants were not of prime importance in this study, this experiment was not performed. See: I. Armitage, L. D. Hall, and A. G. Marshall, *Can. J. Chem.*, **50**, 2119 (1972).

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(12) In the sulfoxides the directly attached aromatic α-carbon resonance is shifted downfield by the greater participation of the inductive effect of the electron-withdrawing nature of the sulfoxide moiety.

Studies on Friedel–Crafts Chemistry. 3. A New Preparative Method of 2-*tert*-Butyl-*p*-xylene by the $AlCl_3$–CH_3NO_2 Catalyzed *tert*-Butylation of *p*-Xylene with 2-*tert*-Butyl- and 2,6-Di-*tert*-butyl-*p*-cresol[1]

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There are few preparatively useful procedures for the synthesis of 2-*tert*-butyl-*p*-xylene (4) by the *tert*-butylation of *p*-xylene (1). The desired compound 4 was only obtained as

Table I. The $AlCl_3$-CH_3NO_2 Catalyzed *tert*-Butylation of *p*-Xylene with 2-*tert*-Butyl- and 2,6-Di-*tert*-butyl-*p*-cresol[a]

Run	Alkylating reagent	Time, min	Product, mol %[b] 2	3	4	5
1	2	1	2.8	36.7	19.3	60.5
2	2	2	0	30.6	16.4	69.4
3	2	5	0	22.6	41.4	77.4
4	2	10	0	20.7	44.8	79.3
5	2	15	0	8.2	39.9	91.8
6	2	20	0	4.1	28.8	95.9
7	2	30	0	3.9	25.0	96.1
8[c,d]	2	17	0	0	60.0[e]	70[e]
9	3	1	0	24.8	20.2	75.2
10	3	2	0	16.4	23.4	83.6
11	3	5	0	6.0	32.7	94.0
12	3	10	0	5.6	36.6	94.4
13	3	15	0	5.5	32.1	94.5
14	3	20	0	4.7	23.7	95.3
15	3	30	0	5.3	26.2	94.7
16[c,f]	3	17	0	16[d]	40.1[e]	77.6[e]

[a] 1/2 or 3: 5 mol/mol. $AlCl_3$-CH_3NO_2/2 or 3: 1.5 mol/mol. Reaction temperature was 1 °C unless otherwise indicated. [b] The yields were determined by GC analyses. [c] In the scale of 53.08 g (0.5 mol) of **1**, this reaction was carried out in order to isolated the desired compound **4**. [d] Reaction temperature, −15 °C. [e] The yields isolated are shown. [f] Reaction temperature, 5 °C.

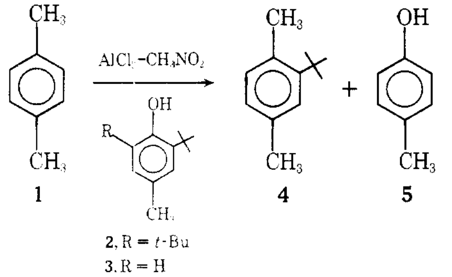
a by-product in low yield in the Friedel–Crafts *tert*-butylation of **1**.[2–4]

It was previously reported that[5] a *tert*-butylating system of $AlCl_3$-CH_3NO_2 catalyst and 2,6-di-*tert*-butyl-*p*-cresol (**2**) was a powerful reagent affording *tert*-butylbenzenes from the corresponding aromatics under very mild conditions (at room temperature, for only 1 min) in good yields.

The above results prompted us to reinvestigate the $AlCl_3$-CH_3NO_2 catalyzed *tert*-butylation of **1** with **2** and 2-*tert*-butyl-*p*-cresol (**3**) in order to obtain **4**, which has never been isolated in good yield, from the Friedel–Crafts *tert*-butylation of **1** as described above.

Results and Discussion

The $AlCl_3$-CH_3NO_2 catalyzed *tert*-butylations of **1** with **2** and **3** were carried out under various conditions, and the results are summarized in Table I.



These reactions were carried out at lower temperature since it was previously shown[5] that when a mixture of three isomers of xylenes was treated with **2** at room temperature in the presence of $AlCl_3$-CH_3NO_2 catalyst, the corresponding *tert*-butyl derivatives of *o*- and *m*-xylene were obtained in good yield, but no **4** was formed and **1** was recovered in almost quantitative yield.

As is shown in Table I, the $AlCl_3$-CH_3NO_2 catalyzed *tert*-butylation of **1** with **2** at 1 °C for 10 min afforded **4** in 44.8 mol % yield,[6] which decreased with increasing reaction time after 10 min. Similarly, the maximum yield of **4** in the reaction with **3** appeared in 10 min reaction time. These results suggest that **4** should be unstable under the conditions used. Indeed, when **1** was treated with **2** at −15 °C in the presence of $AlCl_3$-CH_3NO_2 catalyst, **4** was isolated in 60 mol % yield.

It should be noted that although **2** has two *tert*-butyl groups, the yields of **4** in the reaction with **2** were only somewhat higher than that of the reaction with **3**. These results might suggest that of the two *tert*-butyl groups of **2** only one might mainly act as an alkylating reagent, and the other might be lost as isobutylene. For the practical preparation of **4**, the $AlCl_3$-CH_3NO_2 catalyzed *tert*-butylation of **1** with **3** was carried out on a large scale; **4** was isolated in 40.1 mol % yield.[7]

Although besides the desired product **4** small amounts of the lower and higher boiling products[8] were also detected by gas chromatographic analyses in the respective cases, the detailed determination of the compounds was not carried out. As mentioned above, **4** was isolated first in good yields by the $AlCl_3$-CH_3NO_2 catalyzed *tert*-butylation of **1** with **2** and **3**, respectively.

Experimental Section

All boiling points are uncorrected. NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with Me_4Si as an internal reference.

Analytical Procedures. The analyses were carried out by gas chromatography using a Yanagimoto gas chromatograph, Yanaco YR-101; column, 30% high-vacuum silicon grease, 75 cm; increase rate of column temperature, 8 °C/min; carrier gas, helium at 25 cm^3/min.

From the areas of individual peaks, mole percent figures were calculated for each product after the relative response data had been determined by the internal standard method. Bromobenzene was used as an internal standard.

General Procedure. To a solution of 5 equiv of **1** and 1 mol of **2** or **3** was added a solution of 1.5 equiv of $AlCl_3$ catalyst/equiv of **2** in nitromethane (1 g/2 mL) at a desired and constant temperature. After the reaction mixture was stirred for a specified reaction time at the same temperature, it was poured into a large amount of ice–water. The organic layer was separated and dried over sodium sulfate. A definite amount of bromobenzene was added into the organic layer as an internal standard substance for the gas chromatographic analyses.

Isolation of 4. (a) The *tert*-Butylation with 2. To a solution of 53.08 g (0.5 mol) of **1**, 22 g (0.1 mol) of **2** in 10 mL of nitromethane was added at −15 °C (bath temperature, −17 °C; the catalyst, $AlCl_3$, 19.8 g (0.15 mol) in 40 mL of nitromethane) over a period of 2 min. After the reaction mixture was stirred for an additional 15 min, it was poured into 500 mL of ice–water. The organic layer was separated and washed with 10% sodium hydroxide solution and then with the Claisen alkaline reagent[9] in order to separate **5** and **3** which were formed, respectively.

The remaining organic layer was dried over sodium sulfate and evaporated in vacuo to leave the residue which was distilled under reduced pressure to afford 9.74 g (60 mol %; 30% yield) of **4**: colorless liquid, bp 95–98 °C (18 mm); IR (NaCl) cm^{-1} 2960, 2880, 1465, 1360, 810; NMR (CCl_4) δ 1.36 [9 H, s, $C(CH_3)_3$], 2.26 (3 H, s, CH_3), 2.44 (3 H, s, CH_3), 6.70–7.10 (3 H, m, aromatic protons). The NMR data agreed well with those reported.[4] The washed 10% sodium hydroxide solution was acidified with 10% hydrochloric acid to afford 7.56 g (70 mol %; 70% yield) of **5**.

(b) The *tert*-Butylation with 3. Similarly, to a mixture of 53.08 g (0.5 mol) of **1** and 16.4 g (0.1 mol) of **3** was added at 5 °C the $AlCl_3$–CH_3NO_2 catalyst (19.8 g/40 mL). The reaction mixture was stirred for 15 min and it was treated and worked up as described above to afford 6.5 g (40.1 mol %, 40.1% yield) of **4**, 3.42 g (16%) of the recovered **3**, and 8.38 g (77.6%) of **5**.

Registry No.—**1**, 106-42-3; **2**, 128-37-0; **3**, 2409-55-4; **4**, 42861-84-7; **5**, 106-44-5; $AlCl_3$, 7446-70-0; CH_3NO_2, 75-52-5.

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(6) This value was calculated as follows: amount of **4** (mol)/amount of **2** used (mol) × 100. Therefore, the usual yield of **4** was half of the mol % yield.

(7) In this case, the mol % yield is same as the usual yield.

(8) The products might be the same compounds as reported in the literature.[2-4]

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Novel Photochemically Induced Carbon Monoxide Insertion of an Enone–Iron Tetracarbonyl Complex to Yield a Lactone

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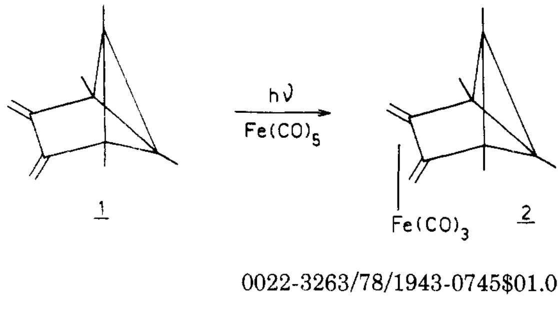
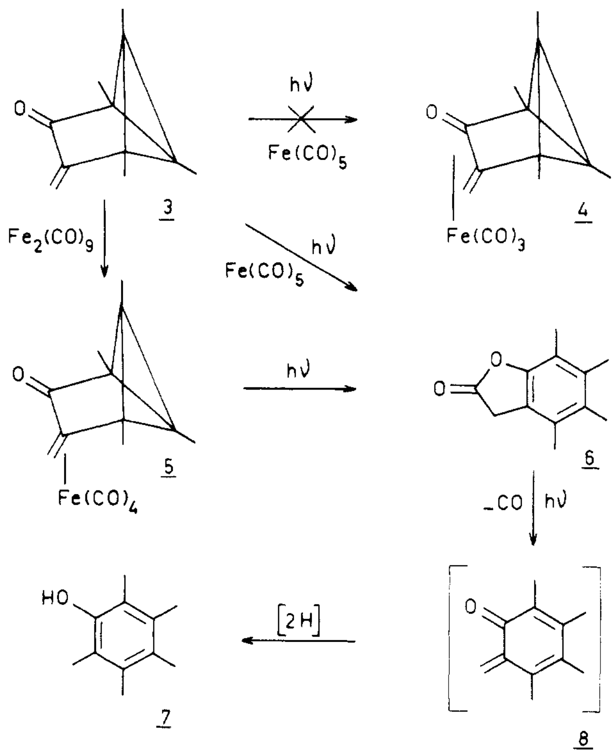
Recently, we reported the synthesis of the bicyclobutane-bridged diene-iron tricarbonyl complex **2** from the corresponding diene **1**[1] (Scheme I). Because both diene **1** and enone **3**[2] show an unexpected reactivity toward the $[Rh(CO)_2Cl]_2$/CO catalyst system[3] and, moreover, because the extremely high reactivity (e.g., in Diels–Alder cycloadditions[4]) of diene **1** can be suppressed by complex formation to iron tricarbonyl, we undertook to prepare the related enone–iron tricarbonyl complex **4**. Unexpectedly, this proved to be impossible and a different reaction, viz., intramolecular CO insertion to yield a lactone, was observed. In view of the current interest in the preparation and properties of enone–iron tetra- and tricarbonyl complexes,[5-8] an account of the results obtained is given herewith.

Following the usual procedure for formation of enone–iron tricarbonyl complexes,[5] enone **3** and iron pentacarbonyl were irradiated in THF solution. However, no iron tricarbonyl complex **4** was isolated, but instead we obtained lactone **6** in 28% yield. IR and ^1H NMR measurements performed during the irradiation showed the presence of small amounts of iron tetracarbonyl complex **5**. Prolonged irradiation in the presence of excess iron pentacarbonyl did not increase the yield of **6**, but formation of substantial amounts of phenol **7**[9] was observed, probably via intermediacy of *o*-quinone methide **8**.[10] (See Scheme II.) Iron tetracarbonyl complex **5** was prepared independently as a yellow oil in 51% yield by treating **3** with diiron nonacarbonyl in THF. On warming at temperatures above 40 °C complex **5** decomposes back to enone **3**. Irradiation of **5** in THF or benzene solution gave lactone **6** in 45% yield but no **4**.[11]

Scheme I

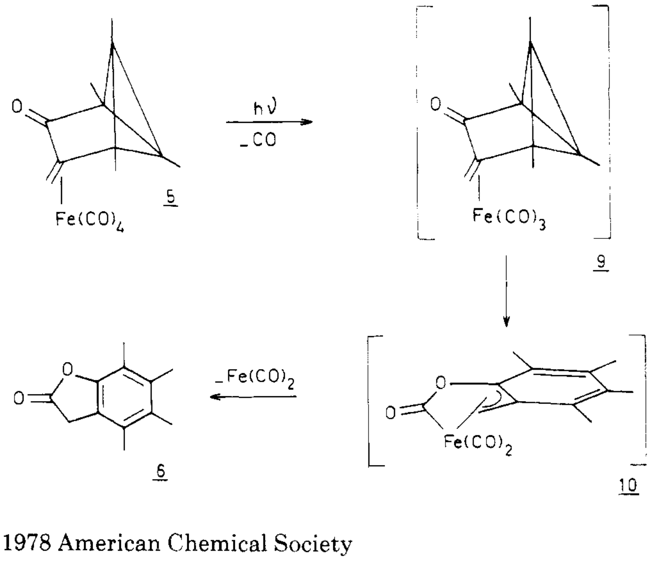


Scheme II



A satisfactory explanation for the unusual photochemically induced reaction of **5** → **6** in comparison with the normal conversion of enone–iron tetracarbonyl into iron tricarbonyl complexes must involve the special nature of the organic ligand. It is conceivable that on irradiation a coordinatively unsaturated complex **9** is formed, which—rather than to complex to the ketone moiety—gives the CO-inserted σ,π-complex **10**, followed by extrusion of the $Fe(CO)_2$ moiety to yield lactone **6** (Scheme III). Subtle differences between the chemical behavior of the iron tetracarbonyl complexes of diene **1** and **3** result in formation of diene complex **2**, on the one hand, and lactone **6**, on the other hand. This may be related to the difference in thermodynamic stability of enone–iron tricarbonyl and diene-iron tricarbonyl complexes.[17]

Scheme III



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