

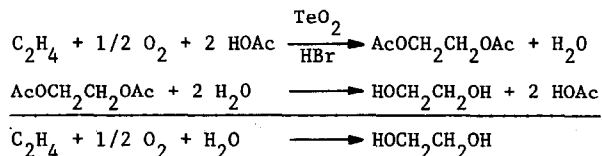
ACETOXYMETHYLATION OF BENZENE, TOLUENE  
AND RELATED COMPOUNDS WITH  $\text{TeO}_2/\text{HOAc}$ \*

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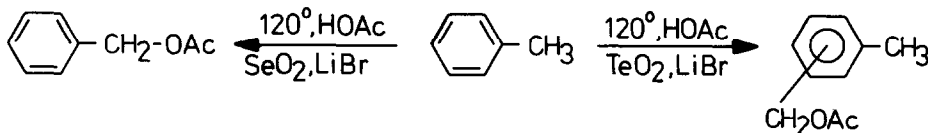
S-100 44 Stockholm 70, Sweden

Catalytic systems containing  $\text{TeO}_2$  and HOAc have attracted considerable attention<sup>1,2</sup> in recent years. Ethylene, for example, can be catalytically converted to ethylene glycol in high yields (95%):



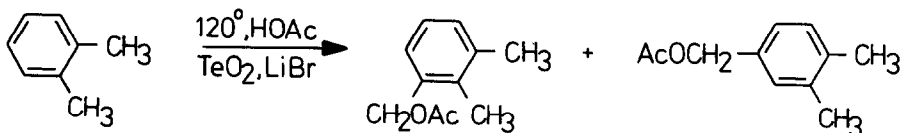
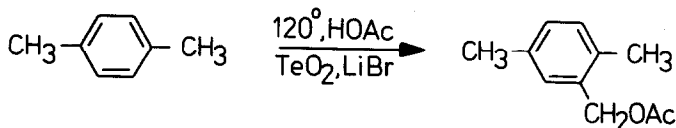
Recently a group at Phillips Petroleum reported<sup>3</sup> that alkyl-substituted aromatic compounds, not unexpectedly<sup>4</sup>, could be catalytically oxidized by a similar procedure. Thus toluene in one example (150 °C,  $\text{O}_2$ , 50 psig initially at 24 °C, HOAc,  $\text{TeO}_2$ , LiBr,  $\text{LiNO}_3$ ) gave benzyl acetate (76% yield) together with small amounts of benzaldehyde (7%), bromo-derivatives (8%) as well as other minor products (partly unspecified).

In this paper we report different results using similar systems (without introduction of pressured  $\text{O}_2$ ).

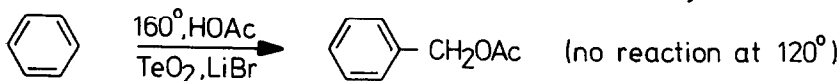


Relative yields<sup>5</sup>: ortho 50%, meta 12%, para 38%

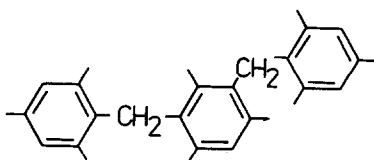
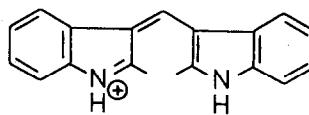
\*Part 2 in the series "Tellurium in Organic Synthesis". For part 1 see ref. 15.

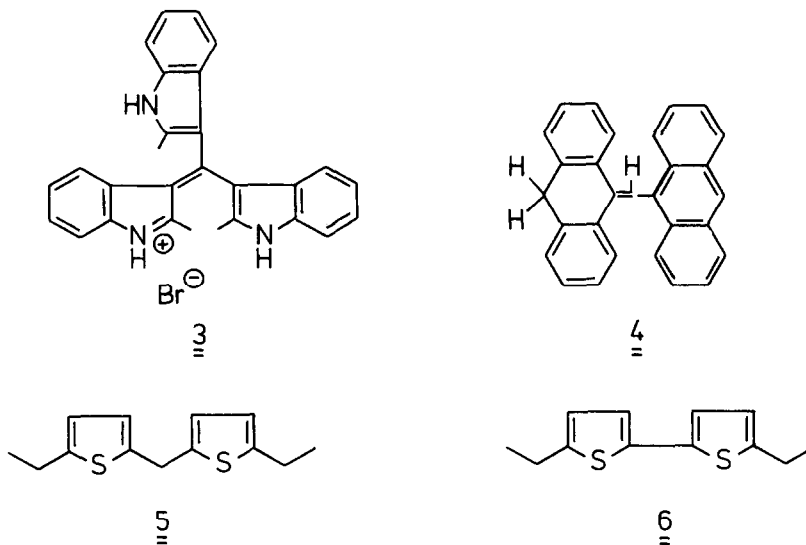


Relative yields: 50 : 50

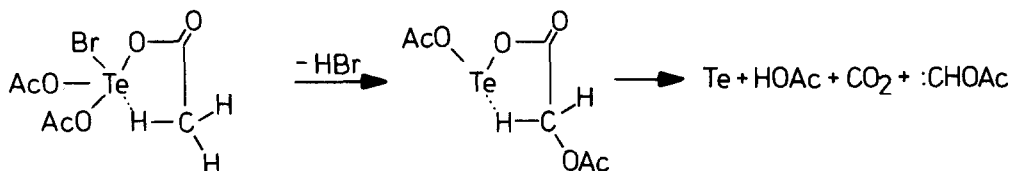


The reactions are clean (no side-chain oxidation was observed) but slow,<sup>6</sup> as contrasted with  $\text{SeO}_2$ . At higher temperatures (e.g. toluene,  $160^\circ\text{C}$ ) diarylmethanes are also formed. The more reactive the hydrocarbons are, the more pronounced are the formation of diarylmethane derivatives, and even more complex compounds. Thus, 1,3,5-trimethylbenzene gave the known trimeric compound 1<sup>7</sup> even at relatively low temperature ( $120^\circ\text{C}$ ). 2-Methylindole gave a mixture of 2 and 3.<sup>8</sup> Anthracene gave 9, 10-anthraquinone together with an isomer and 9-(9-anthrylmethylidene)-9,10-dihydroanthracene (4), which can be isomerized<sup>9</sup> to 9,9'-dianthrylmethane. 2-Ethylthiophene gave the compounds 5 and 6.

1Br<sup>⊖</sup>  
2



Acetoxymethylation of aromatic substrates has earlier been effected with reagents such as  $\text{Mn}(\text{OAc})_3$ <sup>10,11</sup> and  $\text{Pb}(\text{OAc})_4$ <sup>12</sup>. Heiba *et al.*<sup>11</sup> found evidence for a mechanism involving attack by  $\cdot\text{CH}_2\text{COOH}$  on the aromatic ring in the crucial step. Formation of several by-products such as methylation products and arylacetic acids further supported a radical mechanism. However, the absence of such products in the present case and the fact that  $\text{HOAc}$ , when refluxed with  $\text{TeO}_2$  and  $\text{LiBr}$ , slowly yields acetoxyacetic acid<sup>13</sup> and dibromomethane prompt us to suggest the following tentative mechanism:



The active alkylating agent should thus be acetoxy carbene (either free or complexed with  $\text{Te}$ ). Alternatively a reaction pathway involving enolised carboxylate intermediates, as suggested for the conversion of  $\text{Tl}(\text{III})$  carboxylates to  $\alpha$ -acyloxy carboxylic acids, might be operative.<sup>14</sup>

## REFERENCES AND NOTES

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