

The Acetylation of Some Tricarbonyl(alkylbenzene)chromiums

By W. R. JACKSON and W. B. JENNINGS

(Department of Chemistry, Queen's University, Belfast 9)

It has been suggested¹ that tricarbonyl(t-butylbenzene)chromium may be restricted to a conformation (I). In an attempt to investigate possible chemical consequences of such a fixed conformation the acetylation of tricarbonyl-(t-butylbenzene)chromium has been investigated.

Previous work has shown that the isomer distribution obtained by acetylation of tricarbonyl-(toluene)chromium, where relatively free rotation of the tricarbonylchromium group is assumed to be possible, is very different from that of toluene.² We have therefore determined the isomer ratios

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for acetylation of four alkylbenzenes and their tricarbonylchromium compounds.

TABLE

Isomer ratios for acetylations*

Compound	o : m : p ratio		
Toluene	1.2	2	96.8†
Ethylbenzene	0.4	2.9	96.7†
Isopropylbenzene	0.1	3.4	96.5†
t-Butylbenzene	0	4.3	95.7†
Tricarbonyl(toluene)chromium	43	17	40‡
Tricarbonyl(ethylbenzene)- chromium	24	33	43
Tricarbonyl(isopropylbenzene)- chromium	5	59	36
Tricarbonyl(t-butylbenzene)- chromium	0	87	13

* All reactions at 25° in dichloromethane using the acetyl chloride-aluminium chloride complex under nitrogen. Ratios were determined by gas chromatography for alkylacetophenones. The tricarbonyl(alkylacetophenone)chromiums were decomposed and the resulting alkylacetophenones estimated by gas chromatography.

† *cf.* ref. 3 for ratios determined under similar conditions.

‡ *cf.* ref. 2.

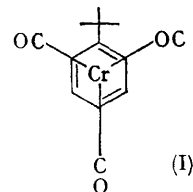
¹ D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *Chem. Comm.*, 1966, 231.

² G. E. Herberich and E. O. Fisher, *Chem. Ber.*, 1962, **95**, 2803.

³ H. C. Brown and G. Marino, *J. Amer. Chem. Soc.*, 1959, **81**, 5611.

⁴ G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Amer. Chem. Soc.*, 1964, **86**, 2203.

The ratios are independent of yields of product (10–30%) and individual isomers do not equilibrate under the reaction conditions.



The high proportion of tricarbonyl(*m*-*t*-butylacetophenone)chromium could be associated with steric hindrance to the departing proton by the superimposed carbonyl groups in the *o*- and *p*-positions. Recent work suggests that bond breaking of aryl C–H bonds is important in the transition state for some acetylations. An attempt is being made to determine partial rate factors in order to explain the results for the other tricarbonyl(alkylbenzene)chromium acetylations.

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