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ALKYLATION OF FURAN CATALYSED BY ARENETRICARBONYLMOLYBDENUM

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Summary

Furan reacted with t-butyl chloride at 130°C in the presence of $ArMo(CO)_3$ to yield 2-t-butylfuran and 2,5-di-t-butylfuran. The catalyst was largely deactivated after 12 h. Up to 150 alkylation events occurred per Mo atom. At low conversions (<10%), using a furan/Mo ratio of 1000/1, the yields of 2-t-butylfuran were high (typically 65—80%). Yields fell sharply with increasing catalyst concentration. Butylation of 2-t-butylfuran occurred more readily than that of furan, and 2,5-di-t-butylfuran was formed in high yield at 30% conversion. Both furan and 2-t-butylfuran reacted with t-butyl chloride more than 50 times as fast as toluene. Evidence is given that the catalytic species do not contain chloride.

Introduction

Successful Friedel—Crafts alkylations of heterocyclic compounds are rare [1]. Resinification of furan, which occurs readily in the presence of Lewis acids, is thought to be the reason why very few alkylation reactions of furan have been reported [2]. Resinification removes furan, and is thought to lead to rapid deactivation of the Friedel—Crafts catalyst through encapsulation. Thus, in marked contrast to homocyclic aromatic compounds, furan has not been reported to undergo alkylation by alkyl halides in yields greater than 10%.

Even in the Friedel—Crafts alkylation of homocyclic aromatics, typically only about ten mol of product are formed per mol of Lewis acid catalyst [3]. Thus, treatment of benzene with t-butyl chloride gave less than seven mol of di-t-butylbenzene per mol of aluminium chloride catalyst [4]. In contrast, White and Farona have described the use of arenetricarbonylmolybdenum $ArMo(CO)_3$ in Friedel—Crafts reactions [5]. These species are highly catalytic and are also reported to be milder and more selective than Lewis acids [6]. The possible use of these molybdenum catalysts for the reaction of furan with t-butyl chloride has now been studied with a view to preparing substituted furans, which are valuable synthetic intermediates [7].

Experimental

Materials. Furan (Aldrich), t-butyl chloride (B.D.H.), toluene (B.D.H.), 1,3,5-cycloheptatrienemolybdenum tricarbonyl, $CHTMo(CO)_3$ (Strem), molybdenum pentachloride (Pfaltz and Bauer) and molybdenum hexacarbonyl (B.D.H.) were used as received. Mesitylenemolybdenum tricarbonyl, $MesMo(CO)_3$, 2-t-butylfuran, and 2,5-di-t-butylfuran were prepared by literature procedures [8,9].

Procedure. Reactions with t-butyl chloride were carried out in glass Carius tubes. Isobutene reactions were performed in an autoclave fitted with a glass liner. Products were determined by GLC (FID) using a 2 m column of 5% E 301.

Results

The Tables record the results of Carius tube reactions. Treatment of furan (1.2 mol) with isobutene (0.6 mol) in the presence of $CHTMo(CO)_3$ (0.4 mmol) in an autoclave at 130°C for 4 h afforded 2-t-butylfuran (3.2 mmol).

Furan (0.4 mol), t-butyl chloride (0.04 mol) and molybdenum pentachloride (0.04 mmol) were heated at 30°C for 1 h but only 0.09 mol of 2-t-butylfuran was detected. No further alkylation occurred on keeping the mixture at 30°C for a further 12 h.

Catalyst turnover, which is defined as the number of alkylating events occurring per molybdenum atom, was calculated using the formula:

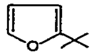
(mol 2-t-butylfuran + 2 × mol 2,5-di-t-butylfuran)/(mol molybdenum catalyst)

Discussion

2,5-Di-substituted furans are useful as precursors of 1,4-diketones [7], but they are not readily prepared from furan. In the absence of direct dialkylation

TABLE 1

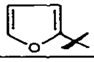
EFFECT OF REACTION TIME AND TEMPERATURE ON REACTIONS OF FURAN (400 mmol) WITH t-BUTYL CHLORIDE (40 mmol) IN THE PRESENCE OF $CHTMo(CO)_3$ (0.04 mmol)

Reaction temperature (°C)	Reaction period (h)	 formed (mmol)	Catalyst turnover
100	12	0.09	2
115	12	0.25	6
130	12	0.89	22
145	12	0.90	22
160	12	0.72	18
130	6	0.63	16
130	18	0.85	21
130	24	0.92	23
130	24	0.13 [a]	3

[a] Catalyst was $MesW(CO)_3$.

TABLE 2

REACTION OF FURAN (75 mmol) WITH t-BUTYL CHLORIDE (300 mmol) IN THE PRESENCE OF VARIOUS MOLYBDENUM CATALYSTS

Catalyst [a] (mmol)	Reaction temperature (°C)	Reaction period (h)	Reactants consumed (mmol)		Products formed (mmol)		Catalyst turnover
				t—BuCl			
A 0.08	130	12	8	11	5.6	0.9	93
A 0.08	130	24	19	18	6.3	1.6	119
A 0.08	130	36	20	26	5.1	1.4	99
A 0.08	130	48	26	40	4.2	1.0	78
A 0.80	130	16	68	35	2.9	3.6	13
B 0.08	130	16	12	28	2.3	0.6	44
C 0.08	130	16	17	22	2.5	0.5	44
A 0.08	140	12	19	33	5.0	0.5	75
B 0.08	140	12	16	20	6.0	0.5	88
C 0.08	140	12	16	21	6.3	0.6	94
C 0.08	130	12	16	20	6.4	2.9	153

[a] A = $Mo(CO)_6$, B = $MesMo(CO)_3$, C = $CHTMo(CO)_3$.

of furan, alkylation in two steps conceivably could afford 2,5-di-alkylfurans.

With a furan/t-butyl chloride ratio of 10/1, similar to the ratio recommended for t-butylation of toluene [5], $CHTMo(CO)_3$ was found to catalyse the formation of 2-t-butylfuran (Table 1). The rate increased with temperature to reach a plateau at 130°C. At this temperature, the catalyst was active for only the first 12 h of reaction. Similar activities were displayed by $CHTMo(CO)_3$, $MesMo(CO)_3$ and $Mo(CO)_6$.

Use of a four-fold molar excess of t-butyl chloride led to formation of both 2-t-butylfuran and 2,5-di-t-butylfuran (Table 2). Again, at 130°C, alkylation was complete within 12 h, at which time there was high efficiency in the utilization of both reactants. Thus, the first entry of Table 2 records yields of t-butylfurans of 81 and 67% based on unrecovered furan and t-butyl chloride, respectively. Such results are unprecedented for the alkylation of furan by means of an alkyl chloride. Reaction times longer than 12 h resulted in degradation of the reactants with little extra alkylation. Catalyst turnover was high and up to 150 alkylation events occurred per Mo atom. Unfortunately, attempts to increase the degree conversion of the reactant by use of higher catalyst loadings resulted only in excessive degradation of the reactants and in low catalyst mileage (Table 2).

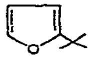
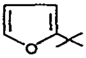
The greater catalyst turnovers observed on increasing the t-butyl chloride/furan ratio agree with the observation that the rate of alkylation of toluene was first order in the concentrations of alkyl halide and molybdenum [5].

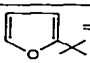
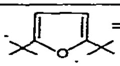
Nature of the catalyst

For homonuclear aromatics, Farona has summarised the evidence that $ArMo(CO)_3$ is the active species or catalyst precursor; apparently, the activity of $Mo(CO)_6$ depends upon formation of $ArMo(CO)_3$ in situ [10]. In the alkylation of toluene, the rate depends markedly on the nature of the arene ring on the catalyst which, therefore, probably remains attached to the molybdenum during the reaction [10]. In the t-butylation of furan, the variation of results

TABLE 3

REACTIONS OF t-BUTYL CHLORIDE WITH FURAN, 2-t-BUTYLFURAN AND TOLUENE IN THE PRESENCE OF $CHTMo(CO)_3$ FOR 12 h AT 130°C

Reactants (mmol)				Catalyst (mmol)	Products (mmol) [a]		Catalyst turnover
		$C_6H_5CH_3$	t-BuCl				
37		37	6.6	0.04	0.63	0.05	18
	20	20	6.6	0.04		1.6	40
	36		6.6	0.04		1.8	45
67			6.6	0.04	0.90	0.01	23
	24		21.6	0.50		7.1 [b]	18

[a] Traces only of t-butyl toluene were detected. [b] Unrecovered  = 9.3 mmol, yield  = 76%.

obtained under supposedly identical reaction conditions was greater than any changes resulting from differences in the catalysts arene ring (Table 2). Possibly, $Mo(CO)_6$ and the various $ArMo(CO)_3$ species tested with furan gave rise to the same active catalyst, perhaps with furan coordinated to the metal.

It has been argued that molybdenum pentachloride is the active species derived from $ArMo(CO)_3$ during alkylation of toluene with t-butyl chloride [11]. There is good evidence that molybdenum pentachloride is not the active species in furan. Thus, although molybdenum pentachloride was highly active at 20°C in t-butyl chloride/toluene mixtures [11], with furan only about 2 mol t-butylfuran was formed per molybdenum atom. As with other Lewis acids, molybdenum pentachloride was rapidly deactivated in furan. Further evidence against involvement of chlorine-containing catalytic species was provided by the observation that $CHTMo(CO)_3$ catalysed the alkylation of furan by isobutene in the absence of any source of chloride.

The formation of 2,5-di-t-butylfuran even at low conversions of furan (see Table 2, particularly the last entry) suggests that the 2-t-butylfuran might undergo alkylation more readily than furan itself. To test this idea and to compare rates of alkylation of furan and homonuclear aromatics, a series of competitive reactions was carried out (Table 3). Both furan and 2-t-butylfuran were alkylated more than fifty times as fast as toluene on treatment of mixtures with $CHTMo(CO)_3$ and t-butyl chloride, but the measurements were not sufficiently accurate to allow the effect of a 2-butyl substituent on the reactivity to be assessed. However, by increasing the catalyst concentration, it was possible to achieve a 30% conversion of 2-t-butylfuran into 2,5-di-t-butylfuran, with a selectivity on furan consumed of 76% (last entry of Table 3). Both the conversion and selectivity in this experiment markedly exceeded those in a comparable reaction with furan (fifth entry of Table 2), which again indicates the more ready alkylation of furan bearing a 2-alkyl substituent.

Although $ArMo(CO)_3$ catalysed the alkylation of furan by t-butyl chloride, the conversions achieved were too low for the reaction to be preparatively useful. With 2-t-butylfuran, however, the molybdenum-catalysed t-butylation could be of value in synthesis.

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