APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 167–172 (1991)

Catalytic ethylation of alkylbenzenes at high pressure

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Study of the catalytic ethylation of *p*-t-butyltoluene in the presence of organosodium compounds, and of toluene in the presence of organopotassium compounds, was carried out at an ethylene pressure of 40 bar.

Various yields of different products were obtained after 23 h of reaction in the presence of different tertiary polyamines used to complex and solubilize the organoalkali compounds.

A higher initial ethylation rate was observed in the presence of organosodium than in the presence of organopotassium species. However, the thermal stability of organopotassium species being higher, much higher yields were observed in their presence in catalytic ethylation reactions than those observed previously.

The results obtained concerning metallation or ethylation of hindered alkylaromatics may be interpreted by an anionic mechanism and the activation by a steric effect.

Keywords: Catalysis, ethylation, organosodium.

1 INTRODUCTION

The catalytic ethylation reaction of arenes at high pressure has been extensively studied by Pines and Stalick.[1]

The catalysts used were the following:

(a) alkali metals (sodium or potassium) dispersed and activated in most cases by *o*-chlorotoluene or anthracene;
(b) alkali metals supported on calcium oxide or graphite.

These authors clearly showed that the ethylation mechanism is anionic. Alkali metals are transformed at high temperatures into alkali salts, either by attack of the chloro compound (the classical reaction for the preparation of organoalkali compounds), or by a metallation reaction via radical anions. The latter reaction has been studied by Petrov *et al.*[2] (metallation of triphenylmethane using the radical anion of the sodium salt of naphthalene) (Scheme 1).

The organometallic compound formed then reacts with ethylene (Scheme 2), the catalytic cycle then completed by the remetallation reaction of compound RH (Scheme 2).

This method of *in-situ* formation of the metallate is not very efficient, at least for the ethylation of alkylaromatics; according to data given by Pines and Stalick,[1] at about 210°C the number of moles of the ethylated product is never much greater than the number of moles of metallic sodium used. It is known that metallation reactions have a poor yield at high temperatures because of competitive reactions (e.g. the Wurtz–Fittig reaction, hydride elimination, etc.).

In-situ production of an undefined quantity of metallate is not very satisfactory from a mechanistic viewpoint and has not enabled the reaction mechanisms to be elucidated.

The Ethyl Corporation (Closson) has patented[3,4] a more direct method of ethylation using 'preformed' organoalkali species.

The catalyst chosen for the ethylation of toluene was benzylsodium and in slightly milder conditions (140°C instead of 210°C), the ethylation yield is much improved: 36 mol of ethylene were consumed per mol of organometallic, i.e. 18 mol per sodium atom.[3,4]

An improvement in yield could also be obtained by the use of benzylpotassium or phenylpotassium instead of the sodium derivative, but the preparation of these species is difficult, because the Wurtz–Fittig coupling reaction takes place preferentially if the potassium dispersion is not fine enough.

On the other hand, Schaap and Pines[5] have shown that, in the presence of potassium and anthracene, a competitive reaction leads to the

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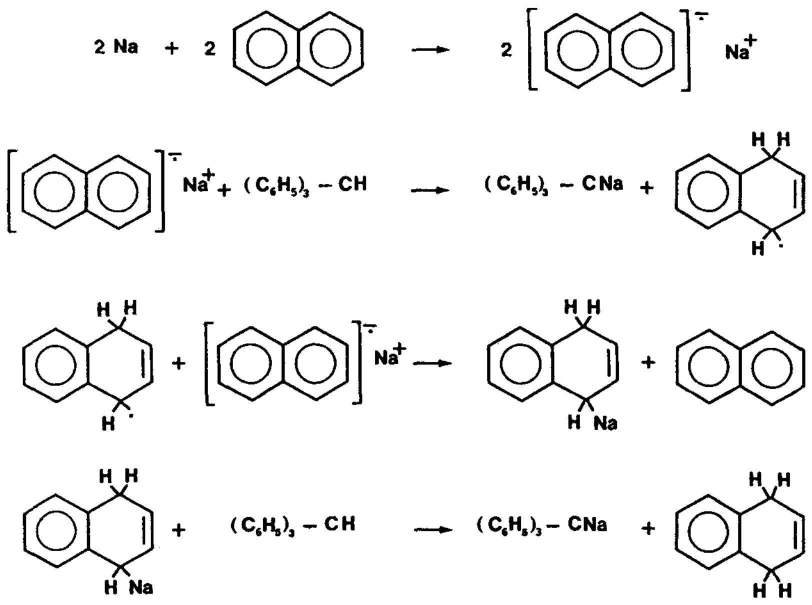
0268-2605/91/030167-06$05.00

Received 14 June 1990
Accepted 1 November 1990



Scheme 1

formation of indane and potassium hydride (Scheme 3).

As will be seen below, ethylation under mild conditions, with preformed metallates chelated with tertiary polyamines, both enables improvement in yields and also allows a theoretical study of the catalytic cycle.

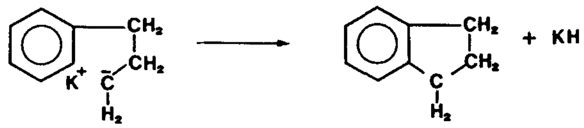
RESULTS

Ethylation in the presence of organosodium compounds

The development of the ethylation reaction of *p*-t-butyltoluene at 85°C and 40 bar is presented in Fig.1 and Scheme 4. It can be seen that after 3 h of reaction, the quantity of ethylene consumed is about 17×10^{-2} mol, i.e. 17 times more than the initial quantity of organosodium (10^{-2} mol of phenylsodium). The reaction appeared to stop at this stage, probably on account of decomposition of the organosodium. The shape of these curves is typically that of a system of consecutive reactions with yields of intermediate products reaching a maximum at about 1 h.

$$\begin{aligned} &\rightarrow RNa + CH_2{=}CH_2 \rightarrow R{-}CH_2{-}CH_2Na \\ &R{-}CH_2{-}CH_2Na + RH \rightleftharpoons R{-}CH_2{-}CH_3 + RNa \end{aligned}$$

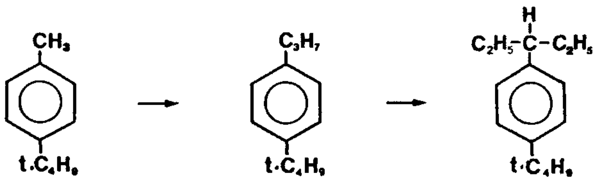
Scheme 2



Scheme 3

The yields of the different products of the ethylation reaction of *p*-t-butyltoluene ($T = 60°C$; $P_{C_2H_4} = 40$ bar) after 23 h of reaction in the presence of different chelating polyamines are given in Table 1.

In this Table, results are expressed in moles of hydrocarbon per mole of phenylsodium initially placed in the vessel. It can be seen that a lowering of the temperature from 85°C to 60°C increases the amount of ethylene consumed (about 56 mol instead of 18 mol in the previous case). The use of 2,2,6,6-tetramethylpiperidine (TMP) does not noticeably change the overall yield, but considerably increases the ratio of diethyl to monoethyl product. This ratio is larger when hexamethyltriethylenetetramine (HMTTA) is used; the initial reaction rate increases considerably



Scheme 4

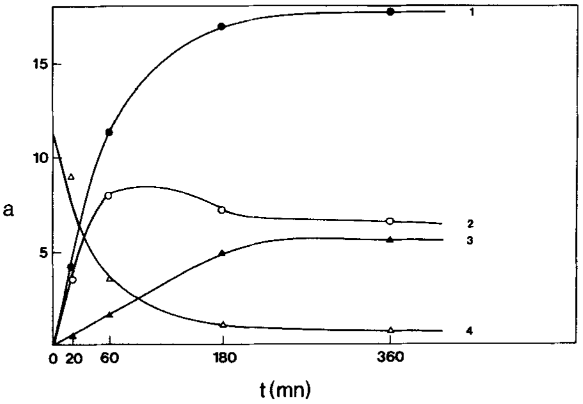


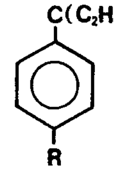
Figure 1 Change in amounts of the products of the ethylation of *p*-t-butyltoluene at 85°C and 40 bar, in the presence of organosodium species chelated by tetramethylcyclohexanediamine (TMCHDA): *a*, no of moles of hydrocarbon per mole of metallate (R^-Na^+); curve 1, ethylene consumed, 2, monoethyl derivative; 3, diethyl derivative, 4, *p*-t-butyltoluene.

(37.9 mol $C_2H_4\,h^{-1}$ per mol of metallate against 4.06 with tetramethylcyclohexanediamine (TMCHDA)).

Ethylation in the presence of organopotassium compounds

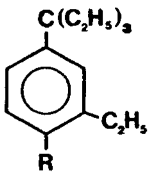
The development with time of the ethylation reaction of toluene at 80°C and 40 bar is shown in Fig. 2. It can be seen that the initial reaction rate is lower than in the presence of organosodium species. But the organopotassium compound is much more thermally stable and the reaction continues even after 23 h. This suggests that the reaction temperature could be increased further. The quantities of ethylene consumed in 23 h, as well as the initial reaction rates obtained, are reported in Tables 1 and 2.

It can be observed that the methyl group on the aromatic is readily triethylated. In two of the runs shown in the Tables, triethylation is towards completion (13.7/18.8 for toluene and 43.4/46 for *p*-t-butyltoluene). Study of the structure of this product by mass spectrometry coupled to a gas chromatograph (GC MS) confirms the formation of 3-ethyl-3-phenylpentane derivatives (**I**).

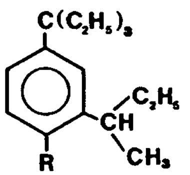


I

When all the benzylic hydrogens of the original hydrocarbon have been replaced by ethyl groups, ethylation continues on the aromatic ring to give tetra- and penta-ethylated compounds whose structure is probably **II** and **III**.



II



III

Unlike with the sodium catalyst, examination of the reaction curves does not show any slowing of the reaction rate with time, this being the case for all five runs carried out in the presence of organopotassium species. Hence, the yields (ethylene consumed in 23 h per mol of metallate) presented in Tables 1 and 2 may not, in this case, be the maximum yields it is possible to reach. These yields are, however, already much higher than those so far reported.

Table 1 Ethylation of *p*-t-butyltoluene at 60°C and $P_{C_2H_4} = 40$ bar[a]

Organo-alkali used	Chelating polyamine	*p*-t-Butyltoluene		Ethylated derivatives after 23 h					Initial reaction rate (mol $C_2H_4\,h^{-1}$)	Reacted ethylene during 23 h
		$t = 0$	$t = 23$ h	Mono-	Di-	Tri-	Tetra-	Penta-		
C_6H_5Na	TMCHDA[b]	46	7.2	21.8	17.0	—	—	—	4.06	55.8
C_6H_5Na	TMCHDA-TMP[c] (2.5:1)	46	16.8	3.6	25.6	—	—	—	2.8	54.8
C_6H_5Na	HMTTA[d]	46	3.9	1.3	38.3	0.19	2.3	—	37.9	87.7
C_6H_5K	HMTTA[d]	46	0.22	0.20	0.46	43.4	0.72	1.04	6.02	139.4

[a] Results expressed as mol of hydrocarbon per mol of metallate. [b] TMCHDA, tetramethylcyclohexanediamine. [c] TMP, tetramethylpiperidine. [d] HMTTA, hexamethyltriethylenetetramine.

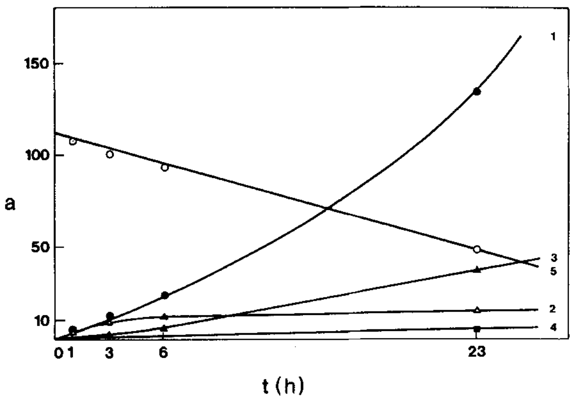


Figure 2 Change in amount of the products of the ethylation of toluene at 80°C and 40 bar, in the presence of organopotassium species chelated by hexamethyltriethylenetetramine (HMTTA): a, no of moles of hydrocarbon per mole of metallate (R^-K^+); curve 1, ethylene consumed, 2, monoethyl derivative; 3, diethyl derivative; 4, triethyl derivative; 5, toluene.

The potassium salt of TMP is also a good ethylation catalyst, due to the fact that it stoichiometrically metallates toluene.

Use of heptamethyltetraethylenepentamine (HMTPA) slightly increases the initial reaction rate and the yield after 23 h.

DISCUSSION

The results presented here on catalytic ethylation have been interpreted using results on equilibrium and metallation rate constants[6] and results on ethylation rate constants.[7] These results confirm that the anomalies previously mentioned by Morton[8] concerning metallation or ethylation of hindered alkyl groups can be interpreted by an anionic mechanism and the activation by a steric effect; Morton suggested that only a radical mechanism (i.e. a single-electron transfer mechnism), could explain these phenomena. We have discussed the kinetic and theoretical aspects elsewhere.[6, 7]

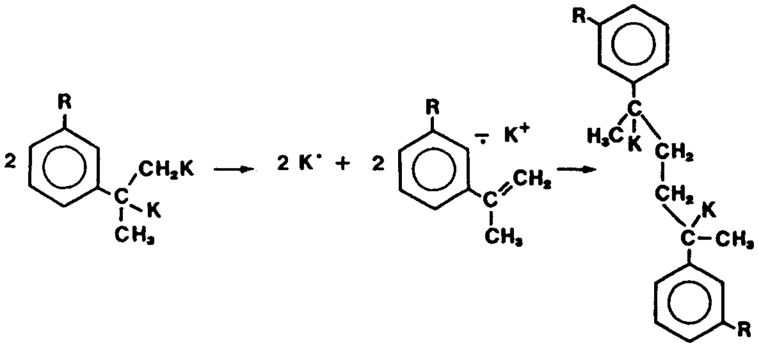
A coupling reaction by a single-electron transfer has however been described by Wilhelm *et al.*[9] This reaction can only take place in the presence of a dimetallate (Scheme 5).

We have never observed the formation of a dimetallate in the reaction medium. Also, the reaction shown in Scheme 5 cannot be catalytic since the alkali metal would precipitate from solution. A detailed study of the kinetic development of a catalytic ethylation has not yet been undertaken: it would be necessary to determine the amount of the intermediate metallated products with time and to determine the ethylation rate constant for each intermediate ethylated product. The qualitative study presented in this work nevertheless gives a relatively clear idea of the mechanism: the initial rate of sodium-catalysed ethylation is generally ten times faster than potassium-catalysed ethylation;[7] this advantage of sodium tends to disappear for the ethylation of very hindered salts (i.e. the progression from the diethylated to the triethylated compound). On the other hand, the equilibrium constant for metallation of hindered hydrocarbons is much lower with sodium than with potassium,[6] so it can be readily understood that potassium is better able to carry out a trisubstitution. Another reason, already mentioned, is that the thermal stability of compounds of the type: α-methylbenzylpotassium C_6H_5—CHK—CH_3 is greater than those of the lithium or sodium analogues, this being linked to the hydride formation

Table 2 Ethylation of toluene at 80°C and $P_{C_2H_4} = 40$ bar[a]

Organo-alkali used	Chelating polyamine	Toluene		Ethylated derivatives after 23 h					Initial reaction rate (mol C_2H_4 h^{-1})	Reacted ethylene during 23 h
		$t = 0$	$t = 23$ h	Mono-	Di-	Tri-	Tetra-	Penta-		
C_6H_5K	HMTTA[b]	113	48.9	14.7	37.3	5.3	3.6	3.2	4.6	135.6
C_6H_5K	HMTTA	18.8	0.78	0.007	0.02	13.7	0.094	4.2	—	62.5
C_6H_5K	HMTTA–TMP[c] (1:1)	75	23.8	11.6	38.2	0.31	0.82	0.42	2.3	94.3
C_6H_5K	HMTPA	226	93.6	50.4	78.2	3.4	0.31	0.13	7.6	218.9

[a] Results expressed as mol of hydrocarbon per mol of metallate. [b] HMTTA, hexamethyltriethylenetetramine. [c] TMP, tetramethylpiperidine. [d] HMTPA, heptamethyltetraethylenepentamine.



Scheme 5

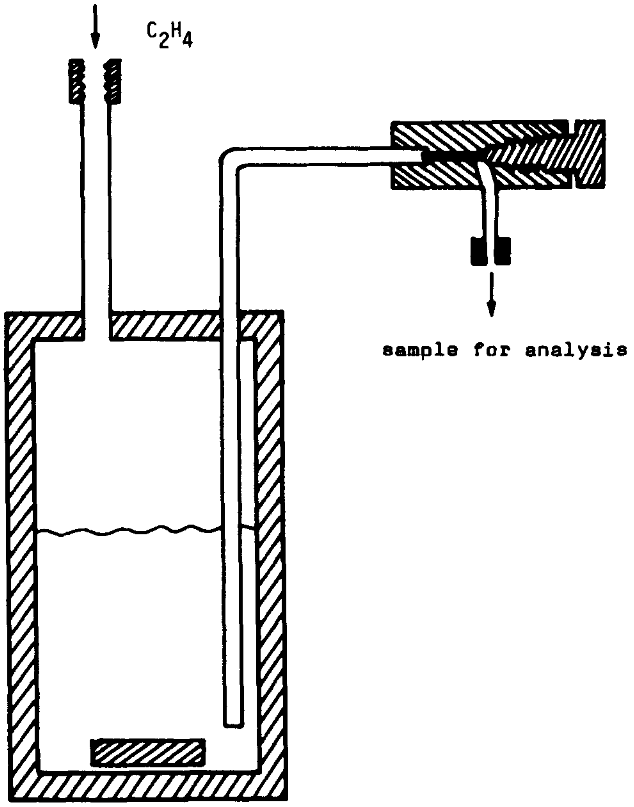


Figure 3 Stainless steel reactor used for high-pressure ethylation.

energy (LiH > NaH > KH). Sodium catalysts thus have an insufficient lifetime for trisubstitution products to be obtained.

EXERIMENTAL

To carry out ethylations of alkylaromatic hydrocarbons at high pressure in ethylene, a stainless-steel vessel was used (capacity 50 cm^3) (Fig. 3). All work was carried out under a nitrogen atmosphere

Ethylation of *p*-t-butyltoluene (exemplification of Fig. 1)

In the vessel swept with nitrogen, 11.5×10^{-2} mol (20 cm^3) of *p*-t-butyltoluene was introduced with 10^{-2} mol (10 cm^3) of a phenylsodium dispersion in decalin[10] and 10^{-2} mol (2 cm^3) of tetramethylcyclohexanediamine (TMCHDA). The mixture was agitated using a magnetic stirring bar. After about 30 min at ambient temperature, the metallate of *p*-t-butyltoluene was formed (p-t-C_4H_9—C_6H_4—CH_2Na, *ca* 10^{-2} mol).

After immersing the vessel in a glycerine bath at 85°C, it was connected to an ethylene cylinder. This was zero time for the reaction. The ethylene pressure was regulated at 40 bar.

Over time, using a nylon tube fitted to a valve at the vessel outlet, under the pressure of the ethylene, samples were immersed in a 0.1 mol dm^{-1} hydrochloric acid solution, contained in a series of test-tubes. The organic phase containing the products of ethylation, among others, was analysed by gas chromatography. The quantities of ethylation products were calculated with respect to decalin introduced as an internal standard into the vessel with the phenylsodium dispersion.

Ethylation of toluene (exemplification of Fig. 2)

To prepare the toluene metallate, 28×10^{-2} mol (30 cm^3) of toluene, 2.5×10^{-3} mol (5 cm^3) of a phenylpotassium dispersion in methylcyclohexane,[11] and 2.5×10^{-3} mol (0.7 cm^3) of hexamethyltriethylenetetramine (HMTTA) were introduced into the vessel swept with nitrogen; 6.3×10^{-3} mol (1 cm^3) of *trans*-decalin was added to the mixture as an internal standard.

The contents of the vessel were agitated using a magnetic stirring bar. At ambient temperature after about 30 min, the metallate of toluene was formed ($\sim 2.5 \times 10^{-3}$ mol of $C_6H_5CH_2K$). Ethylation of the toluene was then carried out using the same procedure as for *p*-t-butyltoluene above.

CONCLUSION

To summarize: the specificity of the organopotassium catalysts results from their high thermal stability and from the fact that activation by the steric effect is more effective for the ethylation reaction than for the demetallation reaction.

It would seem that optimization of the ethylation reaction would involve the combination of different factors, e.g. use of a preformed metallate (already proposed by Closson *et al.*[3,4] for organosodium species), use of a very pure metallate containing the fewest possible Wurtz–Fittig coupling products, and use of pure tertiary amines not possessing any free hydrogen atoms on the nitrogen atoms as chelating reagents (TMCHDA, HMTTA, HMTPA).

REFERENCES

1. Pines, H and Stalick, W S *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*, Academic Press, New York, 1977
2. Petrov E S, Terekhova M I and Shatenshtein A I *Dokl. Akad. Nauk SSSR*, 1970, 192: 1053
3. Closson, R D, Kolka, A J and Liggett, W B US Patents, 2 728 802 (1955), 2 750 384, 2 750 417, 2 751 426 (1956)
4. Closson, R D, Napolitano, J. P, Ecke, G G and Kolka, A J *J. Org. Chem.*, 1957, 22: 646
5. Schaap, L and Pines H *J. Am. Chem. Soc.*, 1957, 79: 4967
6. Assadourian, L and Gau G *New J. Chem.*, 1990, 14: 49
7. Assadourian, L and Gau G *New J. Chem.*, 1990, 14: 57
8. Morton, A A *Solid Organoalkali Metal Reagents*, Gordon and Breech, New York, 1964
9. Wilhelm, D, Clark, T and Schleyer, P R *J. Chem. Soc., Chem. Comm.*, 1983, 5: 211
10. Gau, G and Marques, S *J. Am. Chem. Soc.*, 1976, 98: 1538
11. Gau, G *J. Organomet. Chem.*, 1976, 121: 1