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A Convenient Procedure for Acylation of Alkylbenzenes Using Acid Chlorides-Silver Nitrite

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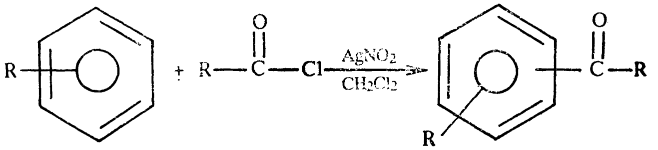
A mild and convenient procedure for acylating electron-rich aromatic compounds such as alkylbenzene was achieved by stirring acid chloride-silver nitrite at room temperature for 72 hrs. We obtained products of acylalkylbenzene in good yield.

The Friedel-Crafts reaction is an effective means of introducing an acyl group into an aromatic ring[1]. The reaction is usually carried out by treatment of the aromatic compound with an acyl halide in the presence of at least one equivalent of a Lewis acid such as $AlCl_3$. Although aluminium chloride is the catalyst most frequently used, many others are also suitable[2]. Catalysts which initiate Friedel-Crafts reactions are all electron acceptors within the classification of acids defined by Lewis[3-5] and include metal halides such as $FeCl_3$, $TiCl_4$, $SnCl_4$ and $ZnCl_2$. Numerous reviews on different aspects of the reaction have been published[2,3], the most extensive being a series of volumes edited by Olah[1]. Lewis acids require anhydrous conditions, since small quantities of water impair their activities as catalysts. Reactions are carried out in especially dried solvents such as carbon disulfide, nitrobenzene or in an excess of the hydrocarbon being acylated[2]. The aim of the present work was to find a new method and effective acylating reagent which is not sensitive to moisture and does not need very dry solvents and could be carried out at room temperature[4] (25.0°C). A recent paper on the iodination of aromatic compounds using silver nitrate and iodine[6] has prompted us to use silver nitrite as an acylating catalyst instead of Lewis acid, and we now report that a mixture of silver nitrite and acid chloride to be suitable for acylation of alkylbenzene (Scheme I).

SCHEME I

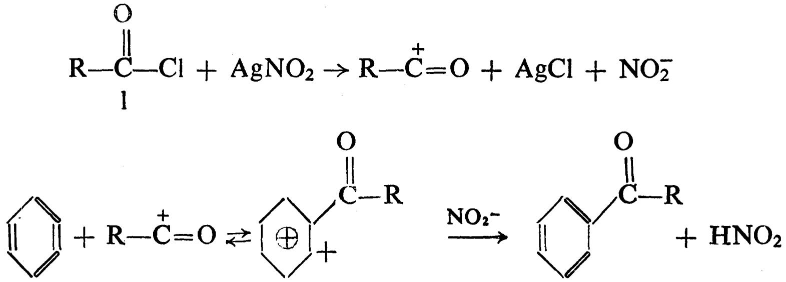


1a R=CH_3 **1b** R=Ph

The acylation of alkylbenzenes using silver nitrite and acetyl chloride (la) or benzoyl chloride (lb) was performed at room temperature in dichloromethane, mono- and di-alkylbenzenes gave monoacyl compounds in good yield; even benzene itself could be acylated, although requiring a longer reaction time. In all the reactions, only one acyl group was introduced into the aromatic ring (Tables 1 and 2). Under similar conditions, anisole gave monoacyl anisole. All the products were identified by GC and ^{13}C NMR (Tables 3 and 4) and characterized by comparisons of their NMR and IR spectra and melting or boiling points with those of authentic samples[7,8] products ratio were determined by GC/MS or NMR. This reaction is very convenient because silver nitrite reacts with the acid chloride producing an acyl carbocation, similar to that proposed for the Friedel-Crafts acylation[9–12]; a silver chloride precipitate[12,13] while NO_2 evolved as brown gas[14] as a result of HNO_2 decomposition (Scheme II).

We have also attempted the alkylation of alkylbenzene promoted by silver nitrite. However, the reaction gave very poor yields because NO_2 reacted with the alkyl carbocations to give the nitroalkanes, thus preventing alkylation of aromatic ring.

SCHEME II



$$R\!-\!\underset{1}{\overset{\overset{\displaystyle O}{\|}}{C}}\!-\!Cl + AgNO_2 \rightarrow R\!-\!\overset{+}{C}\!=\!O + AgCl + NO_2^-$$

1a R=CH_3; **1b** R=Ph

EXPERIMENTAL

General Acylation Procedure : Toluene (461 mg, 5 mM) was added to a mixture of acetyl chloride (391 mg, 5 mM) and $AgNO_2$ (770 mg, 5 mM) at room temperature. The mixture was stirred for 72 hrs. After this time, the white precipitate (AgCl) was removed by filtration and the filtrate was washed with saturated aqueous $NaHCO_3$ and water. After drying over anhydrous Na_2SO_4, the solvent and acetyl chloride were removed under reduced pressure. The product was separated from the unreacted starting meterial by distillation. All products were identified by ^{13}C NMR and GC.

ACKNOWLEDGEMENT

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TABLE 1

ACYLATION OF ALKYLBENZENES WITH SILVER NITRITE AND ACETYL CHLORIDE

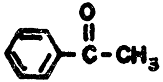
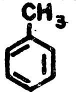
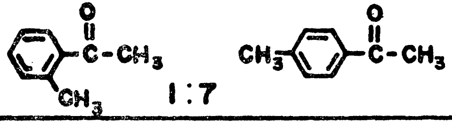
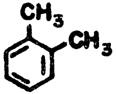
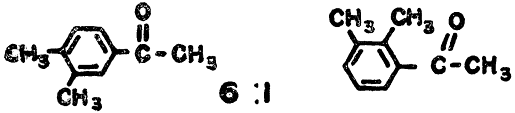
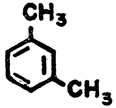
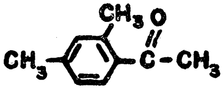
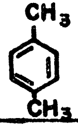
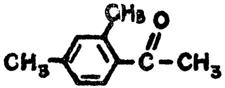
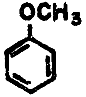
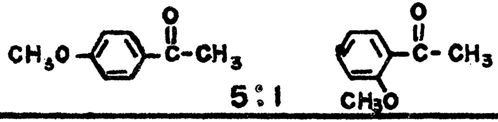
Entry	Starting Material	Time	Isolated Yield %	Products and Ratio
1		72 h	18 %	
2		60 h	47%	 1 : 7
3		70h	60%	 6 : 1
4		60h	40%	
5		72h	45%	
6		48h	70%	 5 : 1

TABLE 2
ACYLATION OF ALKYLBENZENES WITH SILVER NITRITE AND BENZOYL CHLORIDE

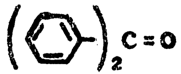
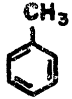
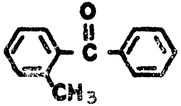
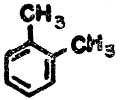
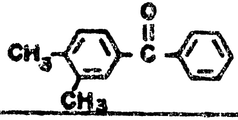
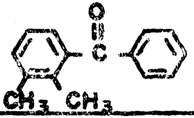
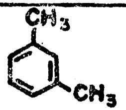
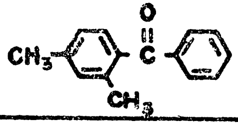
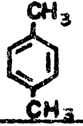
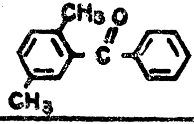
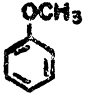
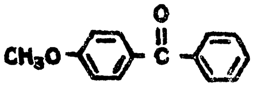
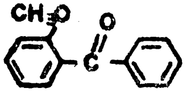
Entry	Starting Material	Time	Isolated Yield %	Products and Ratio
1		75 h	25%	
2		70 h	55%	 5 : 1 
3		73h	75%	 4 : 1 
4		71h	56%	
5		68h	65%	
6		60h	81%	 6 : 1 

TABLE 3

^{13}C NMR DATA FOR ACETOPHENONE DERIVATIVES IN TABLL 1
(in ppm relative to TMS)

Compounds	Aromatic nuclei						
	C=O	C_1	C_2	C_3	C_4	C_5	C_6
Acetophenone	195.63	136.74	128.80	128.80	132.45	128.80	128.80
2-Methylacetophenone	199.25	137.36	137.47	129.13	130.52	125.51	130.55
4-Methylacetophenone	195.46	134.39	127.96	127.89	141.86	127.88	127.88
3,4-Dimethylacetophenone	195.21	139.23	128.44	138.76	142.25	128.82	125.67
2,3-Dimethylacetophenone	201.34	138.66	135.29	137.35	132.34	124.53	124.68
2,4-Dimethylacetophenone	198.61	138.92	134.96	130.63	138.87	125.46	130.74
2,5-Dimethylacetophenone	198.43	136.87	134.26	128.75	129.42	134.63	129.48
4-Methoxyacetophenone	195.36	128.94	129.36	113.98	163.55	113.96	129.36
2-Methoxyacetophenone	197.84	125.63	159.45	112.88	131.97	120.26	129.80

TABLE 4

^{13}C NMR DATA FOR BENZOPHENONE DERIVATIVES IN TABLE 2
(in ppm relative to TMS)

Compounds	Aromatic nuclei						
	C=O	C_1	C_2	C_3	C_4	C_5	C_6
Benzophenone	196.56	136.91	130.62	128.74	131.86	129.13	130.50
2-Methylbromophenone	200.65	138.63	139.22	129.31	133.50	125.9	130.62
4-Methylbenzophenone	196.60	136.21	131.20	125.73	142.20	128.93	130.65
3,4-Dimethylbenzophenone	195.90	135.53	131.21	138.75	142.45	128.66	126.41
2,3-Dimethylbenzophenone	201.52	136.73	139.85	129.82	141.31	125.90	130.75
2,4-Dimethylbenzophenone	199.00	136.22	140.20	130.13	140.54	125.96	130.50
2,5-Dimethylbenzophenone	196.90	139.43	137.25	129.13	133.20	134.63	131.00
4-Methoxybenzophenone	195.10	130.65	131.73	114.32	162.54	114.30	130.70
2-Methoxybenzophenone	198.20	124.20	161.32	113.84	132.92	121.31	131.60

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14. Silver nitrite does not react with the solvent (CH_2Cl_2) because the acyl chloride is more reactive than CH_2Cl_2 towards $AgNO_2$ and the chloride in AgCl comes from the acyl chloride and no alkylation by CH_2Cl_2 observed under these reaction conditions.

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