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The Friedel-Crafts Type Methanesulfonylation of Deactivated Benzenes

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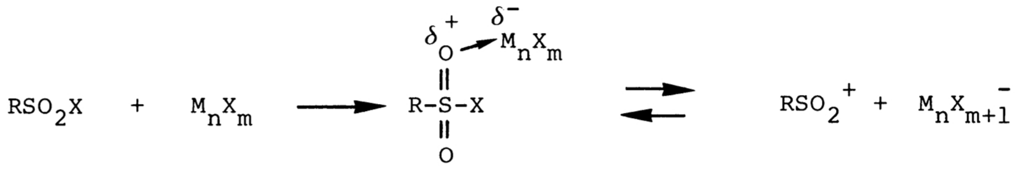
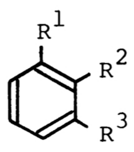
The participation of nonionic donor-acceptor complex [A] was suggested by the analyses of product isolated in the Friedel-Crafts reaction of m-dichlorobenzene with CH_3SO_2Cl in the presence of $AlCl_3$. On the basis of these observations a new practical method of methanesulfonylation of deactivated benzenes employing methanesulfonic anhydride and CF_3SO_3H was developed.

There are several methods of synthesizing methyl aryl sulfones from sulfides, sulfoxides and their derivatives.$^{1)}$ The most practical laboratory method of preparing methyl aryl sulfones is the Friedel-Crafts reaction employing methanesulfonyl chloride, aromatic hydrocarbon and $AlCl_3$ catalyst.$^{2)}$ The structure of electrophilic complexes has been widely discussed,$^{3)}$ and the oxo sulfonium salt [B]$^{4)}$ (Scheme 1) is regarded as a plausible reactive species. However, it is also known that the Friedel-Crafts type methanesulfonylation reactions have serious limitations in particular for certain deactivated benzenes containing halogen or nitro substituents, owing to the electron-withdrawing nature of them.$^{5)}$ In fact, it is reported that the methanesulfonylation of 1a, 1b, and 1c gives the corresponding methyl aryl sulfones in extremely low yield (0-10%), leaving a considerable amount of the starting materials unchanged.$^{6)}$



$$RSO_2X + M_nX_m \longrightarrow R\text{-}\overset{\overset{\delta^+}{O}\rightarrow \overset{\delta^-}{M_nX_m}}{\underset{O}{S}}\text{-}X \rightleftharpoons RSO_2^+ + M_nX_{m+1}^-$$

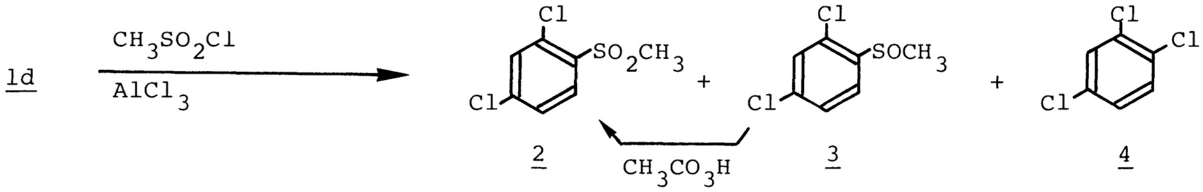
Scheme 1. [A] [B]



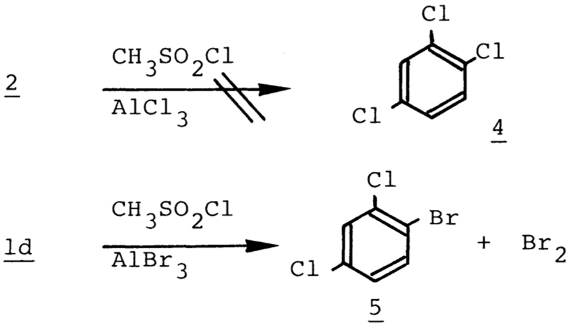
1a: $R^1 = Cl$, $R^2 = R^3 = H$
1b: $R^1 = R^2 = Cl$, $R^3 = H$
1c: $R^1 = NO_2$, $R^2 = R^3 = H$
1d: $R^1 = R^3 = Cl$, $R^2 = H$

In connection with our program in the chemistry of phenolic azo dyes exhibiting a low pKa value,$^{7)}$ we examined in detail the Friedel-Crafts methanesulfonylation of m-dichlorobenzene 1d. On the basis of the analyses of the experimental facts, we found a new practical approach involving heating of methanesulfonic anhydride in the presence of CF_3SO_3H, and the results are presented in this communication.

Treatment of 1d (1.0 equiv.) with methanesulfonyl chloride (0.8 equiv.) in the presence of $AlCl_3$ (0.8 equiv.) without solvents8) gave rise to a mixture of 2,4-dichloro-methylsulfonylbenzene 2 (mp 70-72 °C; 15%), 2,4-dichloro-methylsulfinylbenzene 3 (mp 89-90 °C; 20%), and 1,2,4-trichlorobenzene 4 (35%). The structure of 3 was determined by the following spectral data: MS m/z 208 (M^+); ^1H-NMR δ ($CDCl_3$) 2.75 (s, 3H, CH_3), 7.43 (d, 1H, J=2 Hz, C-3-H), 7.50 (dd, 1H, J=2 and 7 Hz, C-5-H), and 7.91 (d, 1H, J=7 Hz, C-6-H). In addition, 3 was easily converted into 2 on oxidation with CH_3CO_3H at 85 °C.



To our knowledge, the unexpected 3 and 4 are the first products isolated in the Friedel-Crafts methanesulfonylation reaction of dichlorobenzenes. As shown in Fig. 1, the formation of 4 seemed to proceed independently of that of 2. Further reaction of 2 under the same conditions resulted in the recovery of unreacted 2. Moreover, treatment of 1d with methanesulfonyl chloride in the presence of $AlBr_3$ gave 1-bromo-2,4-dichlorobenzene 5 as a sole isolable product, together with gaseous bromine.9)



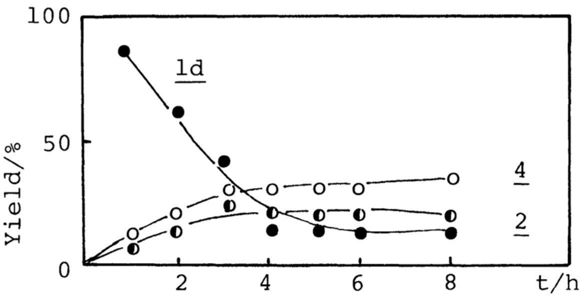
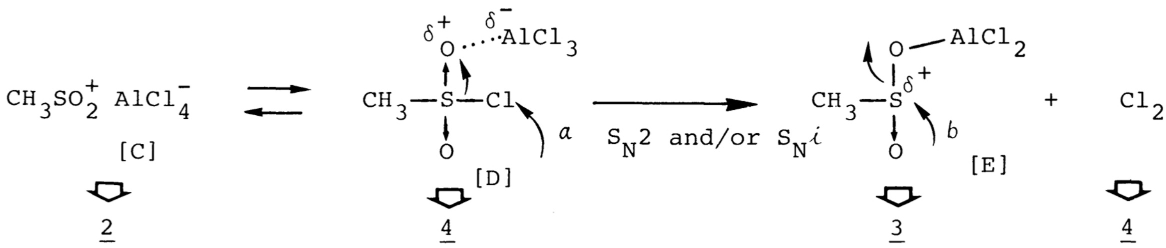


Fig. 1. Yields of 2 and 4 as a function of reaction time.

These observations support the assumption that the formation of 4 is explained in terms of an electrophilic chlorination.10) Owing to the difficulty of generation of an electrophilic centre on the halogen atom (X) of the ionic salt [B], it is considered that the formation of both 3 and 4 preferably derived from the nonionic complex [A] regarded as a transient one. The plausible pathways (a and b) which account for the formation of 3 and 4 are summarized in Scheme 2.

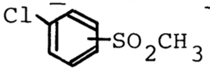
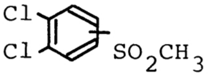
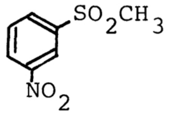
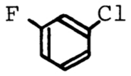
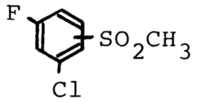
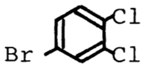
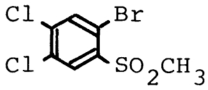
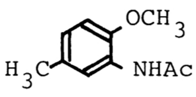
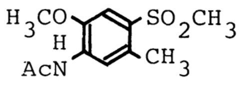
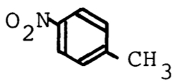
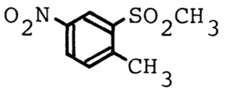
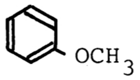
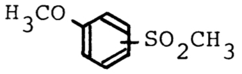


Scheme 2.

The complex [E] leading to 3 would be formed by the electrophilic substitution of 1d with the polarized chlorine atom of the complex [D] (S_N2) and/or by the elimination of Cl_2 from the complex [D] ($S_N i$). In spite of the fact that the Friedel-Crafts sulfonylation is realized as a modification of the acylation reaction,11) it is interesting to note that the behavior of the reaction suggests the intermediary participation of the oxygen-coordinated donor-acceptor complexes [D] and [E].

These findings also indicate the limitation of the Friedel-Crafts sulfonylation by use of alkylsulfonyl chloride in the presence of AlX_3 and led us to the examination of alternative approaches generating no halonium ions. As a results, we found the addition of a catalytic amount of CF_3SO_3H12) in a small excess of methanesulfonic anhydride is effective for methanesulfonylation of 1d (83%) (Table 1, entries 1-5). This procedure is also applicable to other deactivated benzenes and

Table 1. Results of Methanesulfonylation of Deactivated Benzenes with Methanesulfonic Anhydride ($(CH_3SO_2)_2O$)a)

Entry	Substrate	Solvent	Catalyst	Time/h	Temp/°C	Products(Yield/%)
1	1d	$Cl_2C=CCl_2$	H_3PO_4	3	120	no reaction
2	1d	neat	H_3PO_4	3	120	no reaction
3	1d	neat	H_2SO_4	3	120	2 (17) 1d (53)
4	1d	neat	CH_3SO_3H	5	120	2 (37) 1d (52)
5	1d	neat	CF_3SO_3H	3	120	2 (83) 1d (3)
6	1a	neat	CF_3SO_3H	2	100	 (85) -o:-p=1:2
7	1b	neat	CF_3SO_3H	3	90	 (60)
8	1c	neat	CF_3SO_3H	5	120	 (20)
9		neat	CF_3SO_3H	3	90	 (65)
10		neat	CF_3SO_3H	5	140	 (38)
11		neat	CF_3SO_3H	4	90	 (51)
12		neat	CF_3SO_3H	5	120	 (55)
13		neat	CF_3SO_3H	0.5	30	 (85) -o:-p=1:2

a) Prepared *in situ* from $SOCl_2$ (2.0 equiv.) and CH_3SO_3H (5.0 equiv.).

gave the corresponding methyl aryl sulfones in fairly good yields (Table 1, entries 6-12).

A typical procedure is as follows: a solution of methanesulfonic acid (325 cm^3, 5.0 mol) and thionyl chloride (145 cm^3, 2.0 mol) was heated under reflux for 1 h. To the reaction mixture cooled to 25 °C was added 1d (147 g, 1.0 mol) and CF_3SO_3H (8.8 cm^3, 0.1 mol). The whole mixture was heated at 120 °C for 3 h and cooled down to 50 °C, and then poured into ice-water (2 dm^3) and extracted with ethyl acetate (2 x 1 dm^3). The ethyl acetate solution was washed with water (2 x 1 dm^3) and saturated brine (2 x 1 dm^3), dried, and evaporated to leave crude crystals (230 g). Recrystallization from ethyl acetate/hexane (3 : 1) gave pure 2 as white crystals (mp 70-72 °C, 187 g, 83%)

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References

1) A. T. Fuller, J. M. Tonkin, and J. Walker, J. Chem. Soc., 1949, 633; G. B. Barlin and W. V. Brown, J. Chem. Soc., B, 1967, 648; L. Field and R. D. Clark, J. Org. Chem., 22, 1129 (1957).
2) W. E. Truce and G. W. Vriesen, J. Am. Chem. Soc., 75, 5032 (1953).
3) M. Tashiro, Yuki Gosei Kagaku Kyokai Shi, 36, 426 (1978); R. Nakane, ibid., 36, 440 (1978).
4) G. A. Olah and A. M. White, J. Am. Chem. Soc., 89, 3591 (1967); B. Chevrier, J-M. LeCarpentier, and R. Weiss, ibid., 94, 5718 (1972); G. A. Olah, S. Kobayashi, and J. Nishimura, ibid., 95, 564 (1973).
5) A. Schoeberl and A. Wagner, "Houben-Weyl, Methoden der Organischen Chemie," 4th ed, Georg Thieme, Stuttgart (1955), Vol. IX.
6) E. E. Gilbert, J. Org. Chem., 28, 1945 (1963); B. M. Graybill, ibid., 32, 2931 (1967).
7) S. Ichijima and M. Ono, Japan Kokai, 61-184541 (1986).
8) The use of other Lewis acids ($FeCl_3$, $SnCl_4$) and also the use of any solvents with a high boiling point resulted in the recovery of 1d.
9) The formation of Br_2 was also detected in the mixture of CH_3SO_2Cl and $AlBr_3$ even without 1d; For an interesting behavior of the complexes: G. Holt and B. Pagdin, J. Chem. Soc., 1960, 2508.
10) As an example of similar chlorinations: E. C. Dart, G. Holt, and K. D. Jeffreys, J. Chem. Soc., 1966, 1284.
11) F. Klages and F. E. Malecki, Liebigs Ann. Chem., 691, 15 (1966); F. R. Jensen and G. Goldman, "Friedel-Crafts and Related Reactions," ed by G. A. Olah, John Wiley (1964), Vol. 3; G. A. Olah, "Friedel-Crafts Chemistry," Interscience, New York (1973).
12) F. Effenberger, Angew. Chem., 84, 295 (1972).

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