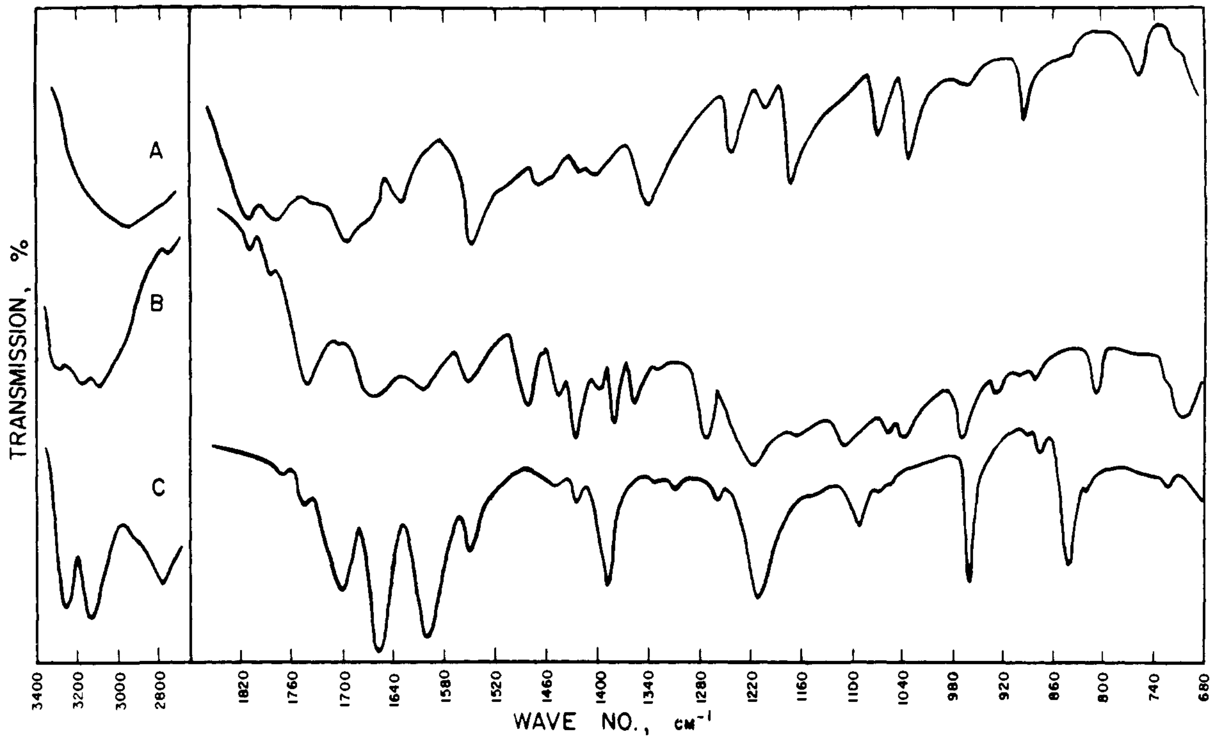

Fig. 3.—Infrared absorption spectra of creatinine hydrochloride (A), creatine ethyl ester hydrochloride (B), and creatine hydrochloride (C). The spectra were measured by E. Wenek with a model 12C Perkin-Elmer spectrophotometer. The solid samples were mulled with hexachlorobutadiene for the region from 2.0–6.0 μ and 6.6–8.0 μ and with Nujol for the region from 6.0–6.6 μ and 8.0–15.0 μ to avoid background absorption. The mulls were supported on sodium chloride plates.

Experimental

Creatine Ethyl Ester Hydrochloride.[7]—This compound was prepared according to the directions of Dox and Yoder.[1] The product melted at 161° (Dox and Yoder, m.p. 163°) when dropped on a preheated melting point block; otherwise, a transformation occurred to give a higher melting compound.

Anal.[14] Calcd. for $C_6H_{14}N_3O_2Cl$: N, 21.48; Cl, 18.12. Found: N, 21.73; Cl, 18.05.

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[14] Analyses were performed by the Microanalytical Laboratory, Squibb Institute for Medical Research, New Brunswick, N. J., under the direction of Mr. J. F. Alicino.

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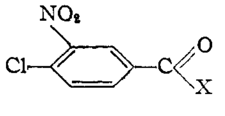
The S_N Mechanism in Aromatic Compounds. XII

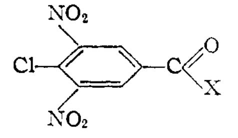
BY JOSEPH MILLER[1]

RECEIVED AUGUST 13, 1954

The activating power of a series of carbonyl 1-substituents in 4-chloro 3-nitro compounds (I)[1] has already been investigated by the author[2] and found to be in the theoretical order, *viz.*, COPh > COMe > CO_2Me > $CONH_2$ > CO_2^- > H. The corresponding 4-chloro-3,5-dinitro compounds (II), with the exception of the acetophenone, have now been investigated, though some react inconveniently fast, and show the same order.



I



II

The results obtained in the present work for replacement of Cl by OMe^- in methanol are given as Table I, which also compares the S.R.F.'s[3] of carbonyl substituents in the mono- and dinitro series. Owing to a combination of fast rates and short temperature range of rate measurements, the Arrhenius parameters for the CO_2Me and COPh compounds are not considered to be very accurate.

Discussion

The approximate independence of aromatic substituent effects is well known, and has also been confirmed for aromatic S_N reactions by earlier results of the author, and various co-workers (quoted in several previous communications). The only real difference here between mono- and dinitro series is a slightly smaller total range of S.R.F.'s in the latter, which is readily explicable on the basis that the over-all –I–T effect should be less effective in the more highly electron deficient ring. The larger value for the S.R.F. of the carboxylate ion and amide in the dinitro series is a consequence of comparisons at different temperatures.

In both series the carbonyl substituents cause a drop in activation energy, as compared with the

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[1] Fulbright Visiting Lecturer/Research Scholar, University of California, Berkeley, for Spring semester 1954.

[2] J. Miller, THIS JOURNAL, **76**, 448 (1954).

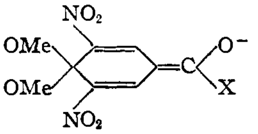
[3] J. Miller, *J. Chem. Soc.*, 3550 (1952).

TABLE I

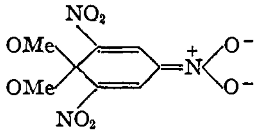
Compound	*Para* substituent	Rate constant (10^5k_2) l./moles^{-1} sec.$^{-1}$ Experimental at temp. in parentheses			Calcd. at 0°	S.R.F. dinitro series (at 0°)	S.R.F. mononitro series (at 50°)	Activation energy, cal.	$\log_{10}$ frequency factor
1-Chloro-2,6-dinitrobenzene[a]	H	90.6 (26.35)	138 (30.2)	226 (35.0)	3.93	1	1	19400	11.1
Sodium 4-chloro-3,5-[a] dinitrobenzoate	CO_2^-	57.0 (0)	686 (26.1)	970 (30.2)	57.0	14.7	7.12	15500	9.2
4-Chloro-3,5-dinitrobenzamide	$CONH_2$	1190 (0)	2920 (9.0)	5390 (15.4)	1190	307	262	15300	10.3
Methyl 4-chloro-3,5-[a] dinitrobenzoate	CO_2Me	3610 (0)	6400 (5.2)	9170 (8.75)	3610	828	1560	16500	11.8
4-Chloro-3,5-dinitrobenzophenone	COPh	2990 4770 (−3.4) (0)	8620 (8.45)	8870 (8.7)	4070	1030	2655	14000	9.7

[a] Recorded in previous communications.[2,3]

parent compounds, of about 4–5000 cal., the effect being bigger for the more activating substituents: some uncertainty in the dinitro series makes the latter less clear-cut. In both series the frequency factor for the carboxylate appears to be definitely low, but no gross and simple effects are apparent for other substituents. All the dinitro compounds with carbonyl substituents (and others not yet reported) develop a red color almost immediately on mixing, though the development is retarded at lower temperatures. This suggests that the products of the reaction, *viz.*, the 4-methoxy-3,5-dinitro compound are involved. This was confirmed by mixing pure products with OMe^- in methanol, when a red color formed at once. The colored compounds almost certainly have the structure III, and are presumably present in equilibrium with the benzenoid compounds and OMe^-. The reversible interaction does not interfere with the over-all reaction which goes to completion, as shown by the agreement of calculated and experimental infinity readings, and also the isolation of pure 4-methoxy 3,5-dinitro compounds direct from the reaction mixtures.



III



IV

The structure III is analogous to that IV assumed for the red compound isolated by Meisenheimer[4] in a more reactive system. No doubt the phenomenon is more general than the visible development of color might suggest, and would be observable in the ultraviolet. It is intended to investigate this at a later date.

Experimental

The measurements were made as in the mononitro series[2]; the rates for the COPh compound at 8.45 and 8.7° being however regarded as a duplicate pair.

Preparation of materials: 1-chloro-2,6-dinitrobenzene as described in footnote 3; 4-chloro-3,5-dinitrobenzoic acid and methyl 4-chloro-3,5-dinitrobenzoate as described in footnote 2; 4-chloro-3,5-dinitrobenzamide m.p. 186° (lit. 186°) as described by Lindemann and Wessel[5]; 4-chloro-3,5-dinitrobenzophenone, m.p. 118° (lit. 118°), as described by Ullmann.[6]

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(4) J. Meisenheimer, *Ann.*, **323**, 242 (1902).

(5) H. Lindemann and W. Wessel, *Ber.*, **58**, 1224 (1925).

(6) F. Ullmann, *Ann.*, **366**, 98 (1909).

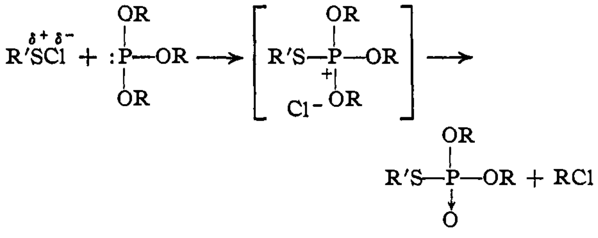
The Reaction of Sulfenyl Chlorides with Trialkyl Phosphites[1]

BY D. C. MORRISON

RECEIVED JUNE 28, 1954

The reaction of various alkyl and acyl halides with tertiary phosphites, with loss of alkyl halide and formation of a phosphonate, has been observed with a large number of alkyl and acyl halides.[2–4] On the other hand, the reaction fails with sulfonyl chlorides and with ester chlorides of sulfuric acid.[2]

In the present work, the reaction of representative sulfenyl chlorides with trialkyl phosphites was studied. In most cases, a very rapid reaction took place, even at Dry Ice temperatures, resulting in esters of monothiophosphoric acid, probably as



$$\overset{\delta+\ \delta-}{R'SCl} + :P(OR)_3 \longrightarrow \left[R'S-\overset{+}{P}(OR)_3\ Cl^-\right] \longrightarrow R'S-P(\rightarrow O)(OR)_2 + RCl$$

This represents a nucleophilic displacement of chloride, accompanied by elimination of alkyl chloride.

The reaction occurred with aliphatic and aromatic sulfenyl chlorides, and with three trialkyl phosphites. Excellent yields of the thioesters were

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(1) The work reported in this paper was aided by a grant to Prof. D. M. Greenberg from the National Cancer Institute, United States Public Health Service (No. C2074).

(2) G. M. Kosolapoff, "Organophosphorus Compounds," Wiley and Sons, Inc., New York, N. Y., 1950, pp. 121–123, 197.

(3) B. C. Saunders, G. J. Stacey, F. Wild and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).

(4) M. I. Kabachnik, P. A. Rossiisskaya and E. S. Shepeleva, *Bull. Acad. Sci. U.R.S.S., Classe. Sci. Chim.*, 163 (1947); *C.A.*, **42**, 4132 (1948).