to point out at this time that this represents still another example of the great utility of the rotatory dispersion technique[6] in the examination of conformational problems.[8]

CARL DJERASSI
L. E. GELLER

Department of Chemistry
Wayne State University
Detroit, Michigan

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[8] C. Djerassi and D. Marshall, *J. Amer. Chem. Soc.* In press; see also Paper XVII, C. Djerassi *et al.*

Kinetics of a nucleophilic replacement of an aromatic nitro group

(*Received* 18 *April* 1958)

SODIUM methoxide reacts with 1:4-dinitronaphthalene in methanol solution to give only the nitrite ion and 4-nitro-1-naphthyl methyl ether. The reaction may be followed by sampling at convenient intervals into toluene and water, with subsequent absorptiometric determination of the nitrite ion in the aqueous phase by a diazotisation–coupling process as described by Rider and Mellon.[1]

The kinetics are of second order, viz.:

$$\text{rate} = k[\text{methoxide}]\,[1{:}4\text{-dinitronaphthalene}]$$

and salt effects appear to be absent. The Arrhenius parameters have been calculated from determinations of the specific rate at six temperatures and are:

$$\text{Activation energy} = 19{\cdot}2 \text{ kcal/g mole}$$
$$\text{Frequency factor } (\log_{10} A) = 11{\cdot}4$$

It is interesting to compare these values with those for *p*-dinitrobenzene, given by Bolto and Miller[2] as 22·4 kcal/g mole and 12·6, respectively.

A. W. BAMFORD
R. W. C. BROADBANK

Leicester College of Technology
and Commerce, Leicester

[1] B. F. Rider and M. G. Mellon, *Industr. Engng. Chem.* (*Anal.*) **18**, 96 (1946).

[2] B. A. Bolto and J. Miller, *Aust. J. Chem.* **9**, 74 (1956).

1-Methoxyvinyl esters*

(*Received* 21 *May* 1958)

WE have found that mercuric salts catalyse the addition of carboxylic acids to methoxyacetylene (I) in methylene chloride solution, the reaction constituting the first general method for the preparation of 1-methoxyvinyl esters† (II). The following examples illustrate the marked catalytic effect of mercuric ions in the formation of II. Whereas the uncatalysed addition of acetic acid (1 mole) to I (2 moles) gave only 25 per cent of IIa (the remainder being anhydride), the addition of 2 mole per cent of mercuric acetate (based on acid) gave 95 per cent IIa. Previous attempts to prepare the analogous 1-ethoxyvinyl acetate have been reported as unsuccessful.[6] In the case of *p*-phenylazobenzoic acid, negligible reaction occurred when a suspension of 1 mole in methylene chloride was

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* Contribution No. 1501 from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

† Until recently,[1–5] 1-alkoxyvinyl esters were not described in the literature.

[1] G. E. Arth, G. I. Poos, R. M. Lukes, F. M. Robinson, W. F. Johns, M. Feurer and L. H. Sarett, *J. Amer. Chem. Soc.* **76**, 1715, 1720 (1954).

[2] R. Broekema, S. van der Werf and J. F. Arens, *Rec. Trav. Chim.* **77**, 258 (1958).

[3] J. C. Sheehan and J. J. Hlavka, *J. Org. Chem.* **23**, 635 (1958).

[4] A. S. Kende, *Chem. and Ind.* 1053 (1956).

[5] F. D. Cramer and K. G. Gärtner, *Chem. and Ind.* 560 (1958).

[6] J. F. Arens and P. Modderman, *Proc. Koninkl. Nederland. Akad. Wetenschap.* **53**, 1163 (1950); *Chem. Abstr.* **45**, 6152*d* (1951); G. Eglinton, E. R. H. Jones, B. L. Shaw and M. C. Whiting, *J. Chem. Soc.* 1862 (1954).

stirred for 12 hr with 2·5 moles of I. However, with the addition of 0·5 and 5 mole per cent of mercuric acetate (based on acid), the reaction was complete in 9, and 1·5 hr respectively, and negligible amounts of anhydride were formed. The 1-methoxyvinyl esters prepared by this general method are recorded in the accompanying table. They all exhibit a sharp band at ca. 5·95 μ in the infrared which is as intense as that due to the ester carbonyl.

The activity of the esters (II) as acylating agents is exemplified by the reaction of a slight excess of IIa with benzylamine (vigorously exothermic); β-naphthylamine (2 hr at 80°); 2,4-dinitrophenol (8 hr at room temperature); and *p*-nitrobenzyl alcohol (3 hr at 80°). After removal of any volatiles, nearly quantitative yields of the acetyl derivatives were obtained. The use of the esters (II) as intermediates in the synthesis of peptides offers attractive possibilities.[3,5]

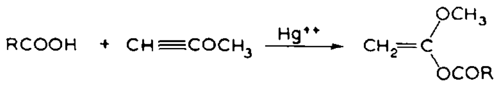
TABLE 1

R	II	Yield (%)*	b.p. or m.p.	Calcd.			Found		
				C,	H,	N or Cl	C,	H,	N or Cl
CH_3	a	75	79° (85 mm)	51·7	6·9		51·8	6·8	
C_6H_5	b	98	95–96° (0·5 mm)	67·4	5·7		67·7	5·8	
p-$NO_2C_6H_4$	c	66	76·5–78°	53·8	4·1	6·3	53·7	4·3	6·4
3,5-$(NO_2)_2C_6H_3$	d	98	93·5–95·5°	44·8	3·0	10·4	45·0	3·2	10·3
p-$C_6H_5N{=}NC_6H_4$	e	80	93·5–94·5°	68·1	5·0	9·9	68·0	5·1	9·9
$(C_6H_5)_2CCl$	f	71	63–63·5°	67·4	5·0	11·7	67·5	4·9	11·5
†	g	85	136·5–137·5°	72·9	9·1		73·3	9·1	

* Although the yields of the crude esters were almost quantitative, some loss resulted in the removal of small amounts of contaminating anhydride.

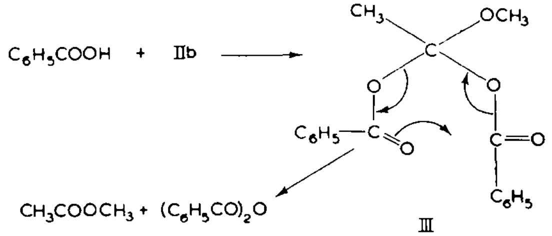
† IIg = 1-methoxyvinyl 3β-acetoxy- Δ^5-bisnorcholenate.

Compounds corresponding to II have been postulated as intermediates in the useful conversion of an acid to its anhydride by I.[6] Indeed, the reaction of acetic acid and benzoic acid with IIa and IIb respectively, gave nearly quantitative yields of the corresponding anhydrides. This conversion undoubtedly occurs by intermediate formation of III, followed by subsequent decomposition to anhydride via a cyclic transition state, rather than by direct attack of acid at the carbonyl carbon atom of II, as the following results show. When 1 mole of IIb was treated with 1 mole of benzoic acid containing 1·06 at. per cent excess ^{18}O per oxygen, benzoic anhydride containing 0·53 at. per cent excess ^{18}O per oxygen was recovered and the methyl acetate concurrently formed was found to contain 0·52 at. per cent excess ^{18}O in the carbonyl oxygen.



$$RCOOH + CH\equiv COCH_3 \xrightarrow{Hg^{++}} CH_2{=}C(OCH_3)OCOR$$

I II



III

Sterling Chemistry Laboratory
Yale University
New Haven, Connecticut

H. H. WASSERMAN
P. S. WHARTON