TABLE III

SUBSTITUTED PHENYL 2-IODOBENZOATES

From betaine	Substituents[a]	M.p., °C.		Analyses of esters, %			
				Calcd.		Found	
		Ester	Phenol[b] (lit.)	C	H	C	H
V	3-NO_2	136–138	95 (95[b])	40.25	2.18	40.50	2.35
VI	2-CH_3-5-NO_2	173–174	116–117 (117[d])	43.86	2.61	43.67	2.90

[a] Substituents in phenyl group of ester and in the phenol derived from it. [b] Ref. 8. [c] Ref. 5. [d] Ref. 11.

fected indirectly as ester formation provides a competitive mode of reaction of the betaines.

Experimental[7]

2-Phenyl Iodoniobenzoate (I), 2-Mesityl Iodoniobenzoate (II), and 2-(*p*-Cyclohexylphenyl) Iodoniobenzoate (III).—Betaines I, II, and III were prepared as described in ref. 3.

2-(2′,4′-Dimethoxyphenyl) Iodoniobenzoate (IV).—To a solution held at 0–5° of 26.4 g. (0.1 mole) of 2-iodosobenzoic acid[3] and 20.7 g. (0.15 mole) of *m*-dimethoxybenzene in 100 ml. of acetic anhydride, there was added slowly 10 ml. of trifluoroacetic acid. After the dark green solution had been stirred at room temperature for 24 hr., there was added with stirring 600 ml. of ether. The iodonium salt was collected as tan crystals and stirred vigorously with 200 ml. of 5 *N* sodium hydroxide solution to give a tan precipitate. This was collected, washed with water, and dried to give 31 g. (81 mmoles, 81%) of **2-(2′,4′-dimethoxyphenyl) iodoniobenzoate (IV)**. Recrystallization from methanol gave colorless crystals, m.p. 234–235° dec. The infrared spectrum showed a carboxylate group absorption band at 1620 cm.$^{-1}$. The nuclear magnetic resonance spectrum showed ring hydrogen absorption bands at τ 1.30 to 3.31 and methoxyl hydrogen absorption bands at τ 6.09 and 6.18.

Anal. Calcd. for $C_{15}H_{13}IO_4$: C, 46.89; H, 3.38; I, 33.03. Found: C, 46.87; H, 3.33; I, 33.16.

The structure of IV was proved by thermal decomposition, which gave as one product 2,4-dimethoxyiodobenzene,[8] m.p. 40° (from hexane), lit.[9] m.p. 40°.

2-(*m*-Nitrophenyl) Iodoniobenzoate (V).—To a solution of 74.4 g. (0.3 mole) of 2-iodobenzoic acid in 300 ml. of concentrated sulfuric acid at 0–5°, there was added over 1 hr. 81 g. (0.3 mole) of potassium persulfate. After the mixture had been stirred at 0–5° for 1 hr., 49.2 g. (0.4 mole) of nitrobenzene was added, and the mixture was stirred at 100° for 3 hr. The cooled mixture was poured into ice–water, and the unchanged nitrobenzene was removed by extraction with benzene. Addition to the aqueous layer of 100 ml. of saturated potassium iodide solution gave pale yellow crystals of crude 2-carboxy-3′-nitrodiphenyliodonium iodide, which were collected. The iodonium salt was stirred vigorously with 200 ml. of 5 *N* sodium hydroxide solution to give a yellow precipitate. This was collected, washed with water, and dried to give 31 g. (80 mmoles, 28%) of **2-(*m*-nitrophenyl) iodoniobenzoate (V)**, m.p. 222–224° dec. Two recrystallizations from ethanol followed by two recrystallizations from chloroform gave colorless crystals, m.p. 229° dec. The infrared spectrum showed a carboxylate group absorption band at 1600 cm.$^{-1}$ and nitro group absorption bands at 1520 and 1340 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_8INO_4$: C, 40.25; H, 2.18; I, 34.42; N, 3.79. Found: C, 40.59; H, 2.24; I, 34.31; N, 3.83.

The structure of V was proved by thermal decomposition, which gave as one product **_m_-nitroiodobenzene**,[8] m.p. 36–38° (from hexane), lit.[10] m.p. 38–39°.

2-(2′-Methyl-5′-nitrophenyl) Iodoniobenzoate (VI).—A mixture of 52.8 g. (0.2 mole) of 2-iodosobenzoic acid,[3] 27.4 g. (0.2 mole) of *p*-nitrotoluene, and 300 ml. of concentrated sulfuric acid was stirred at 100° for 2 hr. After cooling, the mixture was poured into ice–water, and the unchanged *p*-nitrotoluene was removed by extraction with benzene. Addition of 100 ml. of saturated potassium iodide solution to the aqueous layer gave pale yellow crystals of 2-carboxy-2′-methyl-5′-nitrodiphenyliodonium iodide, which were collected. The iodonium salt was stirred vigorously with 200 ml. of 5 *N* sodium hydroxide solution to give a yellow precipitate. This was collected, washed with water, and dried to give 30 g. (78 mmoles, 39%) of **2-(2′-methyl-5′-nitrophenyl) iodoniobenzoate (VI)**, m.p. 207–209° dec. The infrared spectrum showed a carboxylate group absorption band at 1600 cm.$^{-1}$ and nitro group absorption bands at 1520 and 1340 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{10}INO_4$: C, 43.86; H, 2.61; I, 33.19; N, 3.66. Found: C, 43.53; H, 2.64; I, 33.30; N, 3.38.

The structure of VI was proved by thermal decomposition, which gave as one product **2-iodo-4-nitrotoluene**,[8] m.p. 53–54° (from hexane), lit.[11] m.p. 54°.

Reactions of 2-Aryl Iodoniobenzoates.—Thermal reactions of 2-aryl iodoniobenzoates and the reactions of 2-aryl iodoniobenzoates with tetracyclone were run and worked up according to the procedures described in ref. 3. The results are listed in Tables I and II. Esters were hydrolyzed with acid or base to the corresponding known phenols and 2-iodobenzoic acid (Table III).

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(7) Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were taken on a Perkin-Elmer double beam recording spectrophotometer, Model 21, and a Perkin-Elmer Infracord spectrophotometer, Model 137. Ultraviolet spectra were taken on a Cary Model 14 recording spectrophotometer. Nuclear magnetic resonance spectrum was taken on a Varian A-60 high resolution n.m.r. spectrometer. Melting points were taken in capillary tubes and are corrected. Solvents were purified by passage through alumina column and distillation. Reagent grade chemicals were redistilled or recrystallized before used.

(8) The infrared spectrum was identical with that of an authentic sample.

(9) H. Kauffmann and F. Kieser, *Ber.*, **45**, 2333 (1912).

(10) I. R. L. Barker and W. A. Waters, *J. Chem. Soc.*, 150 (1951).

(11) I. Keimatsu and E. Yamazuchi, *J. Pharm. Soc. Japan*, **57**, 992 (1937); *Chem. Abstr.*, **32**, 2519 (1938).

The Infrared Spectra of 1,1-Dinitrocarbanion Salts

LLOYD A. KAPLAN

Organic Chemistry Division,
U. S. Naval Ordnance Laboratory, Silver Spring, Maryland 20910

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Brown[1] has given assignments to the principal infrared absorption bands for the nitro group in various classes of nitro compounds. However, with the exception of the bands at 1151 and 1241 cm.$^{-1}$ reported for the symmetrical and asymmetrical stretching modes, respectively, of the nitro groups in the potassium salt of 1,1-dinitroethane[1] and a report[2] that the anions $H(CH_2)_nC(NO_2)_2^-$, where $n = 0$ to 5 and 9, absorb in the range 1090 to 1157 cm.$^{-1}$ and 1201 to 1251 cm.$^{-1}$ for the symmetrical and asymmetrical stretching modes of the nitro group, there are no assignments given to this functionality in more highly substituted compounds.[3]

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(1) J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

(2) V. I. Slovetski, S. A. Shevelev, V. I. Erashko, A. A. Fainzil'berg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1126 (1962); 57 (1963).

(3) In one other isolated case [L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **25**, 1471 (1960)], the hydrazine salts of ethyl dinitroacetate and dinitroacetohydrazide are reported to absorb at 1133 and 1269 cm.$^{-1}$ and 1124 and 1259 cm.$^{-1}$, respectively.

From the results of various studies carried out in these laboratories,[4] a number of 2- and 3-substituted 1,1-dinitroalkanes and 3-substituted 1,1-dinitro-2-alkene salts were obtained. During the course of these investigations, the infrared spectra of some of these salts were determined and used in characterization. These results, as well as the spectra of a number of previously unreported substituted 1,1-dinitrocarbanion salts, are summarized in Table I.

TABLE I

NITRO GROUP ABSORPTION OF 1,1-DINITROCARBANION SALTS

$^{-}C(NO_2)_2Y$, Y =	Infrared bands	
	1100-1200 cm.$^{-1a}$	1200–1300 cm.$^{-1}$
$-CH_2CHOHCO_2CH_3$	1165 (1130)	1262
$-CH{=}CHCO_2CH_3$	1182	1268
$-CH_2CH_2CO_2CH_3$	1165 (1120)	1245
$-CH_2CHOHCONH_2$	1175 (1132)	1273
$-CH{=}CHCONH_2$	1165	1267
$-CH_2CH_2CONH_2$	1165 (1115)	1260
$-CH_2CHOHCOO^-$	1165 (1115)	1270
$-CH_2CH_2COO^-$	1180 (1112)	1255
$-CH{=}CHNO_2$	1185	1255
$-CH_2CH_2NO_2$	1182 (1140)	1272
$-CH{=}CHCN$	1176	1268
$-CH_3CN$	1190 (1112)	1268
$-CH_2CHOHCOCH_3$	1160 (1120)	1268
$-CH_3$	1150	1240
$-(CH_2)_3CH_3$	1187 (1120)	1248

[a] Values in parentheses represent a second band of about equal or lower intensity.

From the data in Table I, the empirical assignments given to the two bands for the nitro group in substituted 1,1-dinitrocarbanion salts are 1173 ± 10 and 1269 ± 9 cm.$^{-1}$, with maximum deviations of 23 and 22 cm.$^{-1}$, respectively. In most of the saturated derivatives, a second band of about equal or somewhat lower intensity appears in the 1100–1200-cm.$^{-1}$ region. This value is given in parentheses. These bands were not used in the average since they are generally absent in the unsaturated derivatives.

By analogy with the covalent nitro compounds,[1] the 1173-cm.$^{-1}$ band would be due to the symmetrical stretching mode and the 1262-cm.$^{-1}$ band would be due to the asymmetrical stretching mode of the nitro group. This shift in the value of ν_{max} to lower frequencies as compared to the covalent nitro compounds[1] would be expected due to the resonance interaction of the carbanion with the nitro groups.

Experimental

The potassium salts were prepared as described previously.[4] *Extreme caution was exercised in grinding the samples for mull preparation as all of these salts are extremely sensitive to impact and/or friction and may explode during this operation.* Infrared spectra were determined on mulls in Nujol using a Beckman IR-4 spectrophotometer. Individual values of ν_{max} in Table I have an average deviation of 5 cm.$^{-1}$.

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[4] M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 3005 (1961); M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *ibid.*, **26**, 4881 (1961); L. A. Kaplan and M. J. Kamlet, *ibid.*, **27**, 780 (1962); M. J. Kamlet and L. A. Kaplan, *ibid.*, **28**, 2128 (1963); L. A. Kaplan, unpublished results.

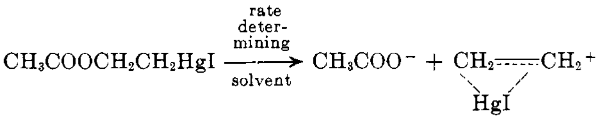
Solvolytic Deoxymercuration Catalyzed by Iodide Ion[1]

MAURICE M. KREEVOY AND MARGARET A. TURNER

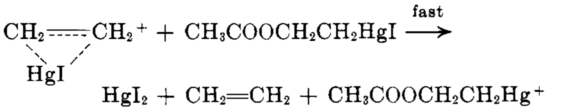
School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota

Received December 17, 1963

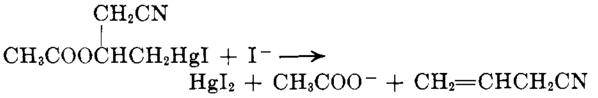
In a previous publication[2] 2-acetoxyethylmercuric iodide has been shown to undergo a solvolytic deoxymercuration, shown in eq. 1 and 2. Acid-catalyzed deoxymercuration has been shown[3] to be subject to cocatalysis by one or two iodide ions,[3] and similar cocatalysis might be expected for solvolytic deoxymercuration. It has now been found in dilute, aqueous solution, for the reaction whose over-all course is shown in eq. 3. This completes the H^+–I^- deoxymercuration system, in the sense that catalysis by zero or one proton; zero, one, or two iodide ions; and all combinations thereof, has now been observed in dilute, aqueous solution. Acid catalysis of the reaction shown in eq. 3 has also been found, but is shown to be insignificant at the pH of the iodide-catalyzed solvolysis.



$$CH_3COOCH_2CH_2HgI \xrightarrow[\text{solvent}]{\text{rate deter-mining}} CH_3COO^- + \underset{HgI}{CH_2\cdots CH_2^+} \quad (1)$$



$$\underset{HgI}{CH_2\cdots CH_2^+} + CH_3COOCH_2CH_2HgI \xrightarrow{\text{fast}} HgI_2 + CH_2{=}CH_2 + CH_3COOCH_2CH_2Hg^+ \quad (2)$$



$$CH_3COO\overset{CH_2CN}{\overset{|}{C}}HCH_2HgI + I^- \longrightarrow HgI_2 + CH_3COO^- + CH_2{=}CHCH_2CN \quad (3)$$

Results

Reactions were carried out at 25°, in aqueous solution containing <2% of methanol. (The substrate was handled as a stock solution in methanol.) Potassium iodide was the source of iodide ion and the acid, where used, was perchloric acid.

The progress of the reaction was followed by following the buildup of the ultraviolet absorption spectrum of HgI_2 and/or its iodide ion complexes, as previously described.[2-4] Substrate concentrations were in the range 10^{-4}–10^{-5} *M* and the iodide ion, when added, was always in at least tenfold excess, so that a first-order rate law was obeyed within each experiment. The integrated form of the first-order rate law, eq. 4, was

$$k_1' = \frac{2.303}{(t - t_0)} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)} \quad (4)$$

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[1] This work was supported by the Air Force Office of Scientific Research through Grant AF-AFOSR-16-63. Reproduction is permitted for any purpose of the U. S. government.

[2] M. M. Kreevoy and G. B. Bodem, *J. Org. Chem.*, **27**, 4539 (1962).

[3] M. M. Kreevoy, R. A. Kretchmer, G. E. Stokker, and A. K. Ahmed, *ibid.*, **28**, 3184 (1963).

[4] M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1099 (1959).