An Investigation of the McFadyen-Stevens Reaction

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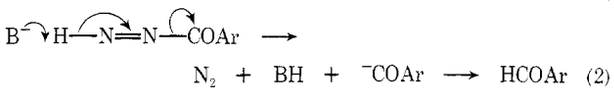
The McFadyen-Stevens reaction of 1-benzenesulfonyl-2-benzoylhydrazines to give benzaldehydes has been shown to proceed with first-order kinetics with respect to the anion of the hydrazine. A Hammett plot gave $\rho = -1.38$ and a deuterium isotope effect of $k_H/k_D = 2.28$ at 160° (equivalent to *ca.* 4.5 at 25°) was obtained. The method provides a convenient and rapid synthesis of 1-deuteriobenzaldehydes. A mechanism is proposed involving a fast reversible α-elimination of sulfinate ion to give an intermediate benzoylaminonitrene, followed by tautomerism of the latter with loss of nitrogen to rearrange to the aldehyde.

The McFadyen-Stevens reaction describes the base-catalyzed thermal decomposition of acylbenzenesulfonhydrazides 1 in ethylene glycol at 160° to give an aldehyde, with loss of nitrogen and sulfinate ion. The intermediary formation of an acyldiimide was suggested by McFadyen and Stevens,[1] and successive bimolecular elimination mechanisms have been put forward for both the first[2] (eq 1) and the second[3] (eq 2) steps of the reaction.

A somewhat related method of preparing aldehydes[4,5] involves the base-catalyzed oxidation of monoacylhydrazides, using potassium ferricyanide[4] or sodium metaperiodate[5] (eq 3).

$$ArCO{-}N{-}NH{-}SO_2Ar \longrightarrow ArCO{-}N{=}NH + ArSO_2^- \quad (1)$$

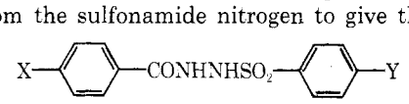


$$B^- H{-}N{=}N{-}COAr \longrightarrow N_2 + BH + {}^-COAr \longrightarrow HCOAr \quad (2)$$

$$ArCONHNH_2 \longrightarrow ArCON{=}NH \longrightarrow ArCHO + N_2 \quad (3)$$

In both reactions the yield of aldehyde is enhanced[1,4] by the presence of ortho,para-directing groups in the 2 or 4 position of the aroylhydrazide moiety, while meta-directing groups in these positions depress the formation of aldehydes[1,6] and lead instead to the symmetrical diacylhydrazides.[6,7] The similarity between these reactions suggested[6] that both occur by a common mechanism. It was therefore proposed[8] that electron-withdrawing substituents Y in the 4 position of the benzenesulfonyl group in 1 might facilitate the elimination step and thereby increase the yield of aldehyde. However, the yield of 4-methylthiazole-5-aldehyde actually *decreased* with the variation in the 4 substituent in the order $CH_3O > H > Br > NO_2$ when a 1-(4-substituted benzenesulfonyl)-2-(4-methylthiazole-5-carbonyl)hydrazine was subjected to the McFadyen-Stevens reaction.[8]

It was postulated,[8] in agreement with a previous proposal,[9] that the initial reaction is the rapid extraction of a proton from the sulfonamide nitrogen to give the anion 2



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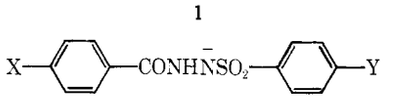
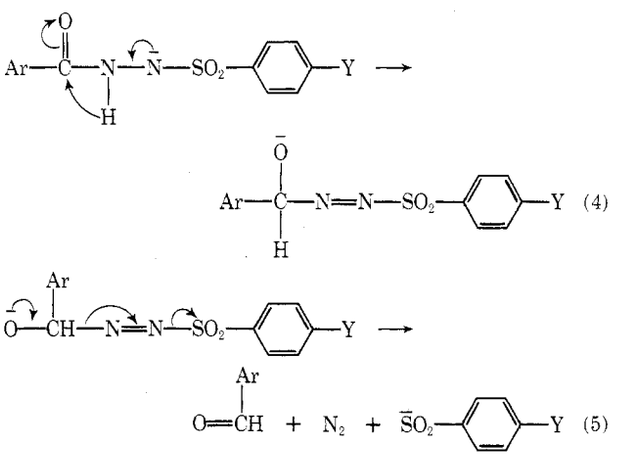


2

and that this anion undergoes a 1,2-hydride shift (eq 4) which would be promoted when Y is electron donating.

The resulting sulfonylazoalkoxide ion could finally decompose[8] (eq 5) to the aldehyde, nitrogen, and arylsulfinate ion by a mechanism which could be regarded as a heterolytic fragmentation[10] of the type a—b—c—d—X → a—b + c=d + X^- which is frequently observed.[10]



$$Ar{-}C(=O){-}N{-}N{-}SO_2{-}Y \longrightarrow Ar{-}C(-O^-){-}N{=}N{-}SO_2{-}Y \quad (4)$$

$$O{-}CH(Ar){-}N{=}N{-}SO_2{-}Y \longrightarrow O{=}CH(Ar) + N_2 + {}^-SO_2{-}Y \quad (5)$$

Earlier reports[1,11] that the method was only applicable to the preparation of aromatic and heterocyclic aldehydes under the standard reaction conditions employing an excess of base (5 equiv) suggested that base-catalyzed attack on the α-hydrogen atom was responsible for the loss of aliphatic aldehydes. This conclusion was confirmed by later experiments[12] extending the reaction to the preparation of aliphatic aldehydes lacking an α-hydrogen atom (*e.g.*, pivalaldehyde[12]). Recent work has shown[13] that when the reaction period is shortened by the use of flash pyrolysis techniques, it is also possible to obtain aliphatic aldehydes possessing one (*e.g.*, isobutyraldehyde) or even two (*e.g.*, *n*-butyraldehyde) α-hydrogen atoms.[13]

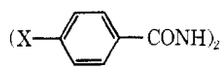
The important observation was made by Newman and Caflisch[14] that when only 1 mol of base was used in the reaction, prolonged reaction periods (up to 35 min) no longer caused a diminution in the amount of benzaldehyde, thus further implicating the excess of base in the decomposition of the aldehydes formed.

Later work[13] suggests that the optimum conditions for the McFadyen-Stevens reaction consists of the use of 1 equiv of base and a relatively aprotic solvent. This is in agreement with the improved procedure of Newman and Caflisch[14] which employs the sodium salt of the mixed hydrazide 1 without additional base. Both groups[13,14] showed that additional base did not increase the yields of aldehyde. Using the sodium salt of 1-benzenesulfonyl-2-(thiophene-2′-carbonyl)hydrazine, we readily obtained thiophene-2-aldehyde under these conditions.

The surface catalysis effect reported by Newman and Caflisch[14] was undetectable in our preparations, the same yield of aldehyde being obtained with or without powdered glass or glass beads. Similar observations have been made

by other workers.[12] It was also noted that the methanesulfonyl analog of 1 (X = OCH_3), *i.e.*, 1-methanesulfonyl-2-(*p*-methoxybenzoyl)hydrazine, functioned as a source of anisaldehyde under the same conditions, albeit with a reduced yield.

The anticipated differences in the acidities of the N-1 and N-2 protons in the 1-benzenesulfonyl-2-acylhydrazines 1 were confirmed by the observation that while the symmetrical diacylhydrazides 3 were totally insoluble in aque-



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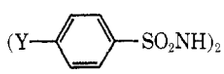
ous alkali at pH 11 or 12, the corresponding symmetrical bis(benzenesulfonhydrazides) 4 as well as the mixed acyl-



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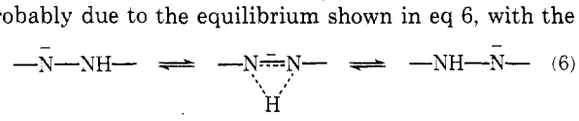
benzenesulfonyl compounds 1 dissolved slowly at pH 11 and rapidly at pH 12. These findings are in good agreement with the conclusions of Underbrink and Lemal[15] that pK_a's of typical sulfonylhydrazines are about 11. The nmr spectrum of the sulfonhydrazide 4 (Y = CH_3), measured in DMSO-d_6, showed aromatic doublets centered at 7.42 (H_B) and 7.72 ppm (H_A), respectively, with J_{AB} = J_{BA} = 9 Hz. Addition of 1 equiv of NaOD in D_2O caused the disappearance of the NH proton signal (singlet at 9.60 ppm), together with an upfield shift of all aromatic protons by 12 Hz to 7.23 and 7.48 ppm (J = 9 Hz). At the same time, the CH_3 signal (singlet) at 2.43 ppm shifted to 2.33 ppm. The changes were reversed on addition of HCl. The sodium salt of 4 (Y = CH_3), prepared using 1 equiv of ethanolic sodium ethoxide, decomposed on standing in solution to give a nitrogen-free product identified as sodium *p*-toluenesulfinate.

The nmr spectrum of the diacylhydrazide 3 (X = OCH_3), in the same solvent, gave aromatic doublets centered at 7.08 (H_B) and 7.97 ppm (H_A), with J_{AB} = J_{BA} = 9 Hz. On the addition of 1 equiv of NaOD and D_2O, no appreciable change occurred in the spectrum apart from the disappearance of the hydrazide NH protons, previously seen as a singlet at 10.28 ppm. There was no change in the position of the methoxy proton signal (singlet) at 3.83 ppm. The mixed hydrazide 1 (X = Y = OCH_3) showed the separate aromatic protons as four discrete doublets (J = 9 Hz) centered at 7.00 and 7.07 (H_B and $H_{B'}$) and 7.77 and 7.83 ppm (H_A and $H_{A'}$), respectively. On addition of 1 equiv of NaOD in D_2O, the NH protons, previously seen as doublets (J = 4 Hz) centered at 9.62 and 10.50 ppm, disappeared and the methoxy signal, previously a sharp singlet at 3.82 ppm, now appeared as two separate peaks at 3.75 and 3.61 ppm. The aromatic proton signals could not be interpreted owing to considerable overlap.

The upfield shift of both the aromatic protons and the methyl group in the bis(benzenesulfonylhydrazide) 4 (Y = CH_3) on addition of 1 mol of NaOD is presumably caused by the shielding effect of the negative charge on the nitrogen in the sodium salt, and the symmetrical distribution is probably due to the equilibrium shown in eq 6, with the



(6)

5

symmetrical form 5 as the predominant species. The nonequivalence of the upfield shift of the two methoxy groups in the mixed hydrazide 1 (X = Y = OCH_3) after addition of 1 mol of base suggests that the structure of the sodium salt of 1 (X = Y = OCH_3) may be 2 rather than the symmetrical form 5.

Table I
Thermolysis of Sodium 1-Benzenesulfonyl-2-acylhydrazines 2 in Diethylcarbitol at 160°

Para substituent X	Para substituent Y	10^4 k, sec^{-1}	Registry no.
OMe	H	23.1	51425-79-7
H	H	9.26	6631-28-3
Br	H	4.73	51425-80-0
OMe	H	10.15[a]	
OMe	OMe	22.8	51425-81-1
OMe	H	23.1	
OMe	Br	24.8	51425-82-2

[a] Made from the N^1, N^2-dideuteriohydrazine.

In order to resolve the ambiguity between mechanisms involving a hydrogen ion or a hydride ion transfer, respectively, the kinetics of solution thermolysis have been studied for the compounds 1 in which X = MeO, H, and Br and Y = H. In presence of 1 equiv of sodium carbonate, their thermolysis at 160° in diethyl carbitol followed first-order kinetics (Table I), and the preformed sodium salts of the hydrazides, obtained by the method of Newman and Caflisch,[14] showed the same rate data as the sodium salts prepared *in situ*. The reaction thus follows first-order kinetics with respect to the anion of the hydrazide.

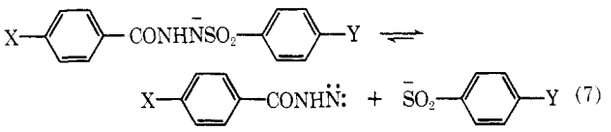
The effect of para substituents on the velocity of the reaction is summarized in Table I; the reaction is seen to be accelerated by electron-donating and retarded by electron-attracting substituents. A Hammett plot gives a ρ value of −1.38, implying that the greatest electron density at the site of reaction is most rate accelerating. This finding clearly speaks against a hydride ion transfer[8] to the carbonyl carbon atom, and suggests instead that the hydrogen is transferred to the carbon as a hydrogen ion. Changing the nature of the para substituent Y did not vary the reaction rates appreciably (*vide infra*).

In order to determine whether the breaking of an X–H bond was involved in a rate-determining step, the N^1,-N^2-dideuteriohydrazide (1, X = MeO, Y = H) was prepared by treatment of a DMSO solution of the protio compound with deuterium oxide. The absence of NH signals in the nmr spectrum showed that complete deuteration had occurred. Decomposition of the sodium salt of the dideuteriohydrazide under standard conditions afforded 1-deuterioanisaldehyde fully deuterated (nmr) in the 1 position.

1-Deuteriobenzaldehyde was similarly prepared in the same isotopic purity, and the method is thus a convenient and rapid route for the synthesis of aromatic 1-deuterioaldehydes.[16] The kinetics of the decomposition of the sodium salt of the dideuteriohydrazide (1, X = MeO, Y = H) showed a considerably slower rate (Table I) for the first-order reaction, with an isotope effect k_H/k_D = 2.28 at 160°. It has been pointed out[17] that the magnitude of the k_H/k_D isotope effect is temperature dependent, decreasing at higher temperatures to a value approaching $2^{1/2}$ or 1.4, and this has been verified experimentally. Using the figures given[17] for the N–H bond, it is possible to calculate that the magnitude of the k_H/k_D isotope effect observed for the McFadyen–Stevens reaction would be *ca.* 4.5 at 25°. The breaking of the N–H bond is therefore clearly implicated in the rate-determining step.

We propose the following mechanism. (a) The reacting species is the anion of the acylbenzenesulfonylhydrazide, probably of structure 2. Proton abstraction from 1 by base

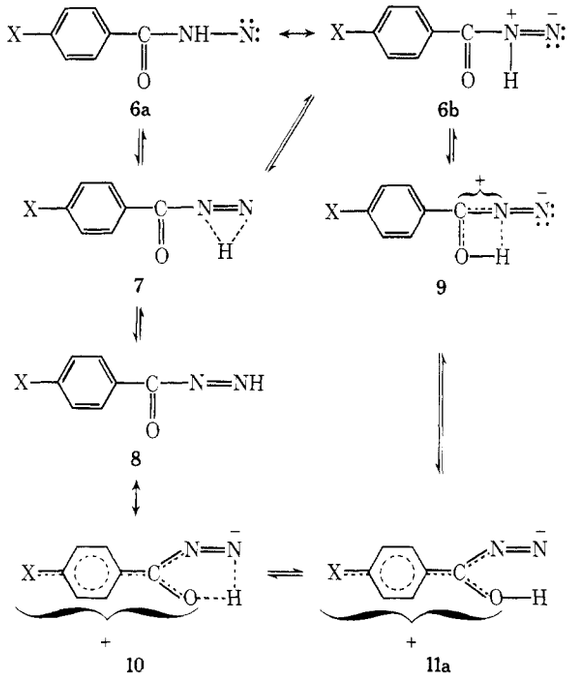
would be extremely rapid. (b) Fast cleavage of the anion **2** occurs by α-elimination of benzenesulfinate ion at the high reaction temperature (160°) to give the benzoylamino-



6a

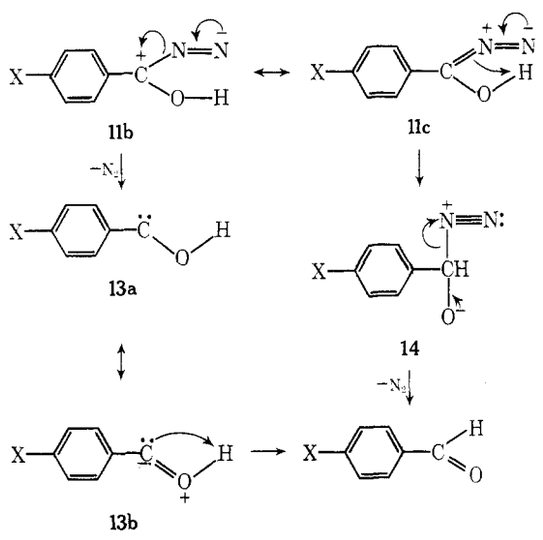
nitrene **6a** (eq 7). Formation of nitrenes by similar α-eliminations has been reported,[18,19] and the base-catalyzed decomposition of 1,1-dialkyl-2-benzenesulfonylhydrazines is known[20-23] to lead to aminonitrenes. Although these species are generally regarded as short lived,[20-23] several benzoylaminonitrenes have recently been prepared and intercepted as crystalline derivatives[24-26] by "trapping" reactions. (c) Insertion of nitrenes into N-H bonds is known to occur.[27,28] The benzoylaminonitrene **6** may undergo a self-insertion reaction into the N-H bond, *via* the intermediate **7**, to give the benzoyldiimide **8** originally postulated by McFadyen and Stevens.[1] This is equivalent to a tautomerization of **6** → **8**, and would be accelerated by the presence of the mesomeric dipolar 1,1-diazene form **6b** of the nitrene,[22,23] in which the repulsion of adjacent positive charges on the carbonyl carbon atom and the N^1 nitrogen atom may be relieved by the rearrangement to **8**. Another way in which this charge repulsion could be relieved would be the formation of the hydrogen-bonded cyclic four-membered transition state **9**, leading to the highly resonance stabilized ylide **11a**, which is also the product of the internal rearrangement of **8**, *via* a five-membered transition state **10** (Scheme I). (d) In contrast to the reversible steps leading to **11a**, the irreversible loss of nitrogen from the mesomer **11b** (Scheme II) will result in the formation of the hydroxyphenylcarbene **13a**, from which migration of the hydroxyl proton to the divalent carbon gives the benzaldehyde directly. This rearrangement will be accelerated, in the dipolar mesomeric form **13b** of the carbene, by the charge repulsion existing between the negative carbene carbon and the negative charge induced at C-1 of the benzene ring by an electron-repelling substituent at C-4 (*e.g.*, OCH_3). This charge repulsion will therefore be relieved by the rapid rearrangement of **13b** to the aldehyde.

Scheme I



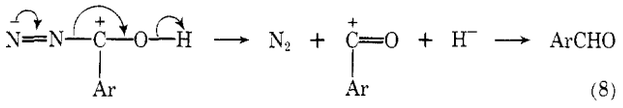
6a **6b** **7** **9** **8** **10** **11a**

Scheme II



11b **11c** **13a** **14** **13b**

If instead of proceeding *via* the hydroxyphenylcarbene **13a** the collapse of the resonance-stabilized ylide **11b** were an a—b—c—d—X type of fragmentation[10] as shown in eq 8, then the effect of para substituents in the aromatic ring



(8)

would be the opposite of that actually observed, and the ρ value would be expected to be positive (hydride ion transfer) instead of negative as found.[29]

The hydroxyphenylcarbene **13**, and its rearrangement to benzaldehyde, have been previously postulated[16] in the preparation of benzaldehyde from benzoylformic acid, where it was demonstrated that the use of benzoylformic acid-d_1 gave 1-deuteriobenzaldehyde. More recently, the analogous hydroxymethylcarbene CH_3-Ċ-OH has been proposed[30] as an intermediate in the formation of acetaldehyde from the reaction of acetic acid with atomic carbon at a liquid nitrogen cooled surface. It was demonstrated that the use of acetic acid-*d* resulted in the formation of 1-deuterioacetaldehyde, suggesting[30] the intermediacy of the carbene CH_3-Ċ-OD.

It should be noted that if the 1-hydroxy-1-phenyldiazoalkane **11c** rearranges by tautomerizing to **14**, this could then undergo a loss of the diazonium leaving group by an intramolecular SN2 attack from the alkoxide ion to give the benzaldehyde directly (Scheme II).

The α-elimination of benzenesulfinate ion (eq 7) is regarded as a fast step for the following reasons. (a) If eq 7 were the rate-determining step, there would be no deuterium isotope effect, since the N-H bond is not broken in this step. However, a deuterium isotope effect of k_H/k_D = 2.28 at 160° was observed. (b) If eq 7 were the rate-determining step, benzenesulfinate ion would be involved in this step, and the nature of the para substituent Y in **1** would have an effect on the rate of the reaction. The kinetics of the reaction were measured for the compounds **1** in which X = OCH_3 and Y = OCH_3, H, and Br, respectively, and under the same conditions as those used to obtain the data in Table I. The results (Table I) show that there is in fact little difference between the rates of the reaction, and the ρ value is +0.14 only.[31] (c) If eq 7 were

Table II[a]
N^1,N^2-Disubstituted Hydrazines R_1NHNHR_2

R_1	R_2	Mp, °C Found	Mp, °C Lit.	Ref	Registry no.
3,4-Dimethoxy-5-benzyloxybenzoyl	Benzenesulfonyl	215–216	215	38	51425-83-3
4-Methoxybenzoyl	Benzenesulfonyl	189–190	190	1	
Benzoyl	*p*-Toluenesulfonyl	174–175	176	39	
Benzoyl	Benzenesulfonyl	170	171	39	
4-Methoxybenzoyl	*p*-Bromobenzenesulfonyl	175–176			
4-Bromobenzoyl	Benzenesulfonyl	200–202			
4-Methoxybenzoyl	4-Methoxybenzoyl	223–225	224–225	40	
4-Methoxybenzoyl	Methanesulfonyl	185–186			51425-84-4
Benzenesulfonyl	Benzenesulfonyl	226–228	228	41	
Thiophene-2-carbonyl	Benzenesulfonyl	198–200			5402-51-7
p-Toluenesulfonyl	*p*-Toluenesulfonyl	242–243	219–220	42, 43	14062-05-6

[a] Satisfactory analytical data (±0.3% for C, H, N, S) were reported for all new compounds. Ed.

the rate-determining step, it would have to be regarded as irreversible. However, if (as it appears) a subsequent step is rate determining, then eq 7 must be a reversible reaction step. In order to verify this critical assumption, a reaction was carried out on the sodium salt of **1** (X = OCH_3; Y = H) under the standard reaction conditions (160°) in ethylene glycol in the presence of 5 molar equiv of sodium *p*-toluenesulfinate. The reaction was stopped after 180 sec, when it was estimated that about 50% of the starting material had reacted. The mixture was separated into aldehyde, *p*-toluenesulfinic acid, and sulfonhydrazide fractions, and the latter fraction was submitted to chemical ionization mass spectrometry. Analysis showed the presence of 7% of **1** (X = OCH_3; Y = CH_3) with a molecular weight of 320, while the remainder consisted of **1** (X = OCH_3; Y = H) with a molecular weight of 306. Under the same conditions, a chemical ionization mass spectrum of **1** (X = OCH_3; Y = H) alone showed no sign of any signal at *m/e* 320. The presence of 7% of **1** (X = OCH_3; Y = CH_3) thus constitutes proof of reversibility of eq 7.

It was found that apart from using diethylcarbitol or ethylene glycol as solvent, the reaction could also be carried out in dimethyl sulfoxide, dimethylformamide, or dimethylacetamide with very similar yields of aldehyde. Thus the sodium salt of **1** (X = OCH_3; Y = H) on heating at 150° in dimethylacetamide gave first-order kinetics with 10^4 k = 29.7 sec^{-1}. The same reaction kinetics and rate constant were obtained when the hydrazide **1** (X = OCH_3; Y = H) was heated with 3 equiv of anhydrous sodium carbonate under the same conditions. This surprisingly small variation in the rates of the reaction, despite the marked differences in the chemical nature of the solvents, is, however, in agreement with typical findings[34,35] for thermolysis reactions in which nitrenes are formed. Since the solvent is presumed to participate in the transition state only by solvation, a nitrene mechanism demands that the reaction rate should vary only little with changes of the solvent.[34,35] In fact, when the sodium salt of **1** (X = OCH_3; Y = H) was heated *without* a solvent at 160° for 1 hr and the aldehyde formed was then collected either by the application of a slight vacuum or by heating to 220°, using a trap cooled to −70°, the yields of aldehyde obtained were of the same order as those using solvents (50–75%).

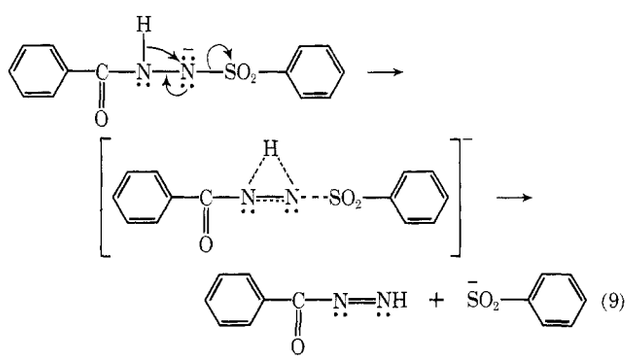
There exists the possibility that the transformation of the anion **2** to the benzoyldiimide **8** could occur in a concerted manner, by a simultaneous 1,2 shift of a hydride ion, expulsion of sulfinate ion, and migration of an electron pair to form the N=N double bond (eq 9), somewhat analogous to the mechanism of the Hofmann rearrangement[9,36] of a bromo amide ion in alkali. However, not only would sulfinate ion be expected to play a bigger role if it were involved in this as a rate-determining step, but also eq 9 could not be expected to be reversible as was demonstrated to be the case for eq 7.

Further investigations of the mechanism of this reaction are in progress.

Table III[a]
Sodium Salts of N^1,N^2-Disubstituted Hydrazines $[R_1NHNR_2]^-Na^+$

R_1	R_2	Molecular formula	Registry no.
4-Methoxybenzoyl	Benzenesulfonyl	$C_{14}H_{13}N_2O_4SNa$	51425-85-5
4-Methoxybenzoyl	4-Bromobenzenesulfonyl	$C_{14}H_{12}BrN_2O_4SNa \cdot 0.25H_2O$	51425-86-6

[a] Satisfactory analytical data (±0.3% for C, H, N, S) were reported for all new compounds. Ed.



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Experimental Section[37]

Preparation of 1,2-Disubstituted Hydrazines. The compounds shown in Table II were synthesized according to published procedures or by the following method. A stirred solution of the monosubstituted hydrazine (0.01 mol) in 12 ml of anhydrous pyridine was treated gradually with the sulfonyl or benzoyl chloride (0.015 mol) at 0° over 15 min. The solution was stirred at room temperature for 1 hr and then poured onto ice-cold 5% HCl. The product was filtered, washed (H_2O), dried (P_2O_5), and recrystallized from 95% ethanol.

Preparation of Sodium Salts of 1,2-Disubstituted Hydrazines. A solution of sodium (0.002 mol) in 2 ml of absolute ethanol was poured under nitrogen into a solution of the 1,2-disubstituted hydrazine (0.002 mol) in 10 ml of absolute ethanol. The solution was left under nitrogen overnight to give the sodium salts in almost quantitative yields (Table III), collected and washed (cold ethanol).

Preparation of N^1,N^2-Dideuteriohydrazines. The 1,2-disubstituted hydrazine (0.003 mol) was dissolved in 3 ml of dry dimethyl sulfoxide, and 2 ml of D_2O (99.7%) was added. The mix-

ture was stirred at room temperature for 2 hr under nitrogen. The product was filtered under nitrogen, washed (D_2O), and dried (P_2O_5). It had the same melting point as that of diprotio starting material. The nmr spectrum (DMSO-d_6) showed the absence of NH protons in the 9.5–10.5 ppm region.

Kinetics of the Reaction. An approximately 0.1 *M* solution of the sodium salt of the 1-benzenesulfonyl-2-acylhydrazine, obtained either by using the preformed sodium salt (0.002 mol) or from a mixture of the hydrazine (0.002 mol) and anhydrous sodium carbonate (1 equiv) in diethylcarbitol (*ca.* 10 ml), was heated in a constant-temperature bath at 160 ± 0.5°. At the end of the reaction period, the mixture was poured into ice and the aldehyde was extracted with ether. The ether extract was concentrated and treated with *ca.* 50 ml (0.0025 mol) of an 0.05 M solution 2,4-dinitrophenylhydrazine in 0.25 *M* methanolic HCl. The yield of aldehyde was estimated gravimetrically. Results of a typical run are given below: a = per cent of aldehyde formed after time t (seconds). Mean values for k were calculated using the method of least squares. The results recorded in Table I were obtained in the same way.

t	60	120	180	240	300	360
a	12.7	24.2	33.5	43.0	50.1	56.2
$10^4 k$	22.65	23.09	22.67	23.43	23.18	22.91
		Mean	23.10			

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References and Notes

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Synthesis of Dioxocarboxylic Acids[1]

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The reaction of ω-halocarboxylates $M^+{}^-OOC(CH_2)_nX$ (II) with disodioacetylacetone (I) was investigated. For II (n = 2; M = Na; X = Cl) and II (n = 5; M = Na; X = Br), no product was isolated. For II (n = 1, 2, 3, 5, 6, and 10; M = Na or Li; X = Cl or Br), except as indicated above, alkylation occurred in 9–92% yields to form the terminal alkylation products (the dioxocarboxylic acids). Overall, lithium salts were superior to sodium salts and ω-bromocarboxylates were better than the chloro compounds.

Plant cuticular lipids contain β-diketones in significant amounts; however, their biosynthesis is poorly understood.[3] One unexplored pathway is the decarboxylation of dioxocarboxylic acids. There is no convenient method for synthesizing acids of this type, although esters of some of these acids have been prepared by a rather cumbersome procedure.[4]

To develop an effective procedure for attaching carboxylic acid chains to β-diketones, we have investigated the reaction of the salts of several ω-halo acids with disodioacetylacetone. In previous work, some alkyl halides have been shown to be highly effective in alkylating dianions of this type selectively at the terminal position[5,6] (eq 1). In

$$\underset{\text{I}}{CH_3C(\overset{Na^+}{\overline{C}}H)C(=O)\overset{Na^+}{\overline{C}}H_2} + RX \longrightarrow \xrightarrow{H^+} CH_3COCH_2COCH_2R \quad R = \text{methyl, ethyl, butyl, etc.} \quad (1)$$

the present investigation it was found that alkylation of the dianion of 2,4-pentanedione (I) at the terminal posi-