

TABLE I

N-Chlorosulfonyl β -lactam prepared from	β -Lactam	Yield, %	Ref
2,3-Dimethyl-2-butene (a)		92	5
2-Methyl-2-butene (b)		98	5
Methyleneecyclohexane (c)		98	
1,3-Cyclooctadiene (d)		97	
Norbornene (e)		77	3
1,3-Butadiene ^a (f)		72	2
Isoprene ^a (g)		68	2

^a N-Chlorosulfonyl lactam was not isolated.

lactam band at 5.53 μ . Nmr absorption was at δ 1.0–2.8 (10 H) and 3.05 (s, 2 H).

Anal. Calcd for $C_8H_{12}ClNO_2S$: C, 40.4; H, 5.05; N, 5.90. Found: C, 40.17; H, 5.05; N, 5.82.

Reaction of N-Chlorosulfonyl β -Lactams with Na_2SO_3 .

General Procedure.—A solution of N-chlorosulfonyl β -lactam dissolved in ether was added slowly to a stirred mixture of about two parts 25% aqueous sodium sulfite and one part ether. The aqueous phase was kept slightly basic by addition of 10% KOH solution as the reduction proceeded. The reaction course could easily be followed by thin layer chromatography in which the product had a considerably smaller R_f value than the starting material. At the end of the reaction (usually less than 15 min) the ether layer was separated and dried and the solvent evaporated. The products were of greater than 95% purity as determined by nmr. The reduction could be carried out either at 25 or 0°.

1-Aza-2-keto[6.2.0]bicyclodec-8-ene.—N-Chlorosulfonyl β -lactam (2.25 g) was dissolved in 15 ml of ether and added to a mixture of 5 ml of ether and 10 ml of 25% aqueous sodium sulfite. The aqueous phase was kept between pH 7 and 8 by addition of 10% KOH solution. After 15 min the showed the absence of starting material and the formation of only one ether soluble product. The ether layer was separated and dried and the solvent was evaporated to yield 1.32 g (97%) of solid. Recrystallization from ethanol gave colorless granules: mp 100–101°; ir ($CHCl_3$) 5.71 μ ; nmr ($CDCl_3$) δ 1.2–2.4 (8 H), 3.2–3.6 (1 H), 4.4–4.7 (1 H), 4.2–5.0 (2 H), and 6.8–7.2 (1 H).

Anal. Calcd for $C_{10}H_{12}NO$: C, 71.5; H, 8.60; N, 9.26. Found: C, 71.12; H, 8.62; N, 9.10.

1-Azaspiro[3.5]nonan-2-one was prepared as above in 98% yield: colorless oil; bp 123° (4.2 mm); ir ($CHCl_3$) 5.72 μ ; nmr ($CDCl_3$) δ 1.3–2.0 (10 H), 2.61 (d, $J = 1.5$ cps, 2 H, collapses to singlet on addition of D_2O), 7.3–8.0 (broad singlet 1 H).

Anal. Calcd for $C_9H_{13}NO$: C, 69.00; H, 9.34; N, 10.07. Found: C, 69.33; H, 9.39; N, 10.00.

Registry No.—Table I—lactam a, 17060-95-6; b, 24571-92-4; c, 24571-93-5; d, 24571-94-6; e, 24571-95-7; f, 22937-11-7; g, 20012-93-5; sodium sulfite, 7757-83-7; 1-azaspiro[3.5]nonan-2-one, 24571-98-0; 1-aza-2-keto[6.2.0]bicyclodec-8-ene, 24571-99-1.

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Evaluation of the σ^* Parameter for Halodinitromethyl Groups

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Hine and Bailey¹ have determined the Taft σ^* parameter for a number of polynitroalkyl groups and noted that the value of σ^* for the trinitromethyl group, 4.54, is the largest recorded for an electrically neutral substituent. In connection with other studies, we required the σ^* values for fluoro-, chloro-, and bromodinitromethyl substituents. We have evaluated the σ^* parameter for these substituents by measuring the rates of reaction of the corresponding 4-halo-4,4-dinitrobutyric acids with diphenyldiazomethane in ethanol at 30°. These data are summarized in Table I.

TABLE I

RATE OF REACTION OF 4-Z-4,4-DINITROBUTYRIC ACID WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 30°

Z	$k, M^{-1} \text{min}^{-1}$
F	3.56 ± 0.04
Cl	3.36 ± 0.16^a
Br	3.18 ± 0.03

^a 2.97 ± 0.03 at 25°.

From these specific rate constants and the equation¹

$$\log k = -0.105 + 1.174 \sigma^*$$

we obtained σ^* values for the 3-halo-3,3-dinitropropyl functions (Table II). Though the error in the value

TABLE II

TAFT σ^* PARAMETERS

R	σ^*
$FC(NO_2)_2CH_2CH_2$	0.559 ± 0.005
$ClC(NO_2)_2CH_2CH_2^a$	0.537 ± 0.017
$BrC(NO_2)_2CH_2CH_2$	0.517 ± 0.004
$FC(NO_2)_2^b$	4.4
$ClC(NO_2)_2^b$	4.2
$BrC(NO_2)_2^b$	4.1

^a $\sigma^* = 0.538 \pm 0.005$ from 25° data. ^b By multiplying σ^* for $ZC(NO_2)_2CH_2CH_2$ by (2.8)².

of k at 30° for 4-chloro-4,4-dinitrobutyric acid is unexplainedly about four times larger than that for the fluoro and bromo acids, measurements of the specific rate at 25° afforded a much more precise value of the rate constant for the chloro acid (Table I). Calculating σ^* for the 3-chloro-3,3-dinitropropyl function from the 25° data gives a value which is essentially identical with the one obtained from the 30° rate data.

Experimental Section

Preparation of 4-Halo-4,4-dinitrobutyric Acids.—The fluoro acid, prepared by hydrolyzing the corresponding methyl ester,² was obtained as colorless needles, mp 37–38°.

Chlorination and bromination of potassium methyl 4,4-dinitrobutyrate in pentane afforded methyl 4-chloro- and methyl 4-

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bromo-4,4-dinitrobutyrate, respectively. The crude esters were hydrolyzed to the corresponding acids by refluxing with constant-boiling hydrochloric acid for 8 hr. Recrystallization of the crude acids from water gave 4-chloro-4,4-dinitrobutyric acid as a granular, white solid, mp 95.4–96.2°.

Anal. Calcd for $C_4H_6ClN_2O_6$: C, 22.6; H, 2.4; N, 13.2; Cl, 16.7. Found: C, 22.8, 22.9; H, 2.5, 2.4; N, 12.6, 12.5; Cl, 17.1, 16.8.

The 4-bromo acid, mp 90–91° (lit.³ mp 88–89°), was obtained as glistening white plates.

Kinetic Procedure.—Measurements of the rates of reaction of these acids with diphenyldiazomethane were carried out as described previously.⁴ The data summary in Table I results from at least five kinetic runs for each substrate.

Registry No.—4-Chloro-4,4-dinitrobutyric acid, 24057-18-9; 4-fluoro-4,4-dinitrobutyric acid, 15895-15-5; 4-bromo-4,4-dinitrobutyric acid, 5029-14-1; diphenyldiazomethane, 883-40-9.

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An Unusual Aspect of the Dimerization of N-Vinylcarbazole by Redox Reactions. The Participation of Molecular Oxygen

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The remarkable atypical features of polymerization on N-vinylcarbazole by either an ionic or a free-radical process have been recorded in a number of recent investigations. For example, it is difficult to present an adequate mechanism for the commercial preparation of poly-N-vinylcarbazole employing sodium chromate in hot aqueous dispersion or to account for the following observations when π -complex electron acceptors such as *p*-chloranil, tetracyanoethylene, and trinitrobenzene were used as initiators:^{2,3} water (which normally inhibits ionic polymerization), thiophene (a potent retarder of conventional cationic propagation), and acrylonitrile (a material readily polymerized by radical or anionic species) each have qualitatively no effect on the polymerization of N-vinylcarbazole.

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Also, it has been noted that conventional free-radical polymerization of this monomer initiated by azobisisobutyronitrile is sensitive to oxygen but unaffected by the presence of oxygen when π -complex electron acceptors are used as initiators.⁴ Further, highly hindered phenols such as 2,6-di-*t*-butylphenol and 2,4-di-*t*-butylphenol, powerful inhibitors of free-radical chain reactions, do not retard but rather accelerate the azobisisobutyronitrile-initiated polymerization of N-vinylcarbazole in methanol.⁵

In an earlier study we have reported that ferric nitrate initiated polymerization of N-vinylcarbazole and 4-vinylpyridine proceeding by a one-electron transfer process⁶ and that a dimer of N-vinylcarbazole, *trans*-1,2-dicarbazylcyclobutane, was among the products.⁷ In extension of this study we have examined the reaction between N-vinylcarbazole and hydrogen peroxide, a redox couple analogous to the interaction between dimethylaniline and benzoyl peroxide,⁸ which also afforded the dimeric product, *trans*-1,2-dicarbazylcyclobutane.

During the course of this investigation, we have found evidence of molecular oxygen participation in the formation of this dimer when either ferric nitrate or hydrogen peroxide is employed as an oxidant. In this note we wish to report our recent findings and suggest a role for molecular oxygen in the reaction sequence.

When reaction mixtures containing 5.0 mmol of N-vinylcarbazole and 0.05–0.5 mmol of ferric nitrate (hydrate) in methanol–water medium (9:1 v/v) were stirred at room temperature under nitrogen atmosphere over a period of 4 hr, they furnished some poly-N-vinylcarbazole of rather low molecular weight and a trace amount of dimer. The hydrolysis products of the monomer, carbazole, and acetaldehyde isolated as its 2,4-dinitrophenylhydrazone derivative were found to be the major products. In open air, for the same period of time, it afforded the same dimer in 15–20% of the theoretical yield in addition to the hydrolysis products. Under a stream of oxygen with 0.05–0.5 mmol of ferric nitrate the yield of the dimer was raised to 37–40%. Parallel observations were obtained when hydrogen peroxide was used as oxidant under comparable conditions. Under a nitrogen atmosphere, the yield of the dimer was practically nil with concentrations of hydrogen peroxide varying from 0.057 to 0.57 mmol. The bulk of the yield was found to be the hydrolysis products. In the presence of oxygen the dimer was obtained in 15–17% yield. The concentration of hydrogen peroxide in these reactions has no effect on the yield of the dimer. It is apparent that oxygen is not used in the regeneration of the oxidants but nevertheless essential in the formation of the dimer. It seems necessary for us to reexamine the mechanism of the dimer formation which we proposed in one of our earlier reports.

The interaction of molecular oxygen with free radicals is well known. The formation of the peroxy radical by oxygen with the intermediary radicals in this sequence of transformations should result in the forma-

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