alumina. Elution with C_6H_6 gave yellow crystals which was recrystallized from EtOH to give **7** (417 mg, 34%), mp 153—154°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1735, 1720 and 1695. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 251 (4.26), 289 sh (4.10), 299 (4.17), 363 (4.23). NMR (in $CDCl_3$) τ: 1.6—1.8 (2H, m, H_5 and H_8), 2.11 (1H, d, $J=16$ Hz, $\text{-C}\underline{\text{H}}\text{=CHCO}_2\text{Me}$), 2.5—3.2 (2H, m, H_6 and H_7), 3.66 (1H, d, $J=16$ Hz, $\text{-CH=C}\underline{\text{H}}\text{CO}_2\text{Me}$), 5.97, 6.08 and 6.17 (3×3H, 3×s, 3×OMe). Mass Spectrum *m/e*: 317 (M^+). *Anal.* Calcd. for $C_{16}H_{15}O_6N$: C, 60.56; H, 4.77; N, 4.41. Found: C, 60.78; H, 4.85; N, 4.27.

Ethyl 3-Methylindolizine-1-carboxylate (8)——According to a previously described procedure,[4] a solution of α-bromopropionaldehyde (1.4 g) and ethyl 2-pyridineacetate (3.3 g) in acetone (10 ml) was heated under reflux for 14 hr. Work-up yielded a yellow oil, which was purified by preparative thin-layer chromatography on alumina to give **6** (900 mg, 47%). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1670. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 229 (4.57), 232 (4.57), 250 sh (3.79), 257 (3.91), 265 (3.87), 304 sh (3.97), 312 (4.09), 343 (3.95) and 353 (3.95). NMR (in $CDCl_3$) τ: 1.82 (1H, d, $J=9$ Hz, H_8), 2.28 (1H, d, $J=7$ Hz, H_5), 3.00 (1H, s, H_2), 2.8—3.5 (2H, m, H_6 and H_7), 5.65 (2H, q, $J=7$ Hz, $\text{-C}\underline{\text{H}}_2\text{CH}_3$), 7.50 (3H, s, Me) and 8.61 (3H, t, $J=7$ Hz, $\text{-CH}_2\text{C}\underline{\text{H}}_3$).

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On the Scavenging of Azido Radicals by Nitroso Compounds

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No electron spin resonance (ESR) evidence has ever been put forward on the azido radical ($N_3\cdot$) in both solid and solution phases, although an unstable ultraviolet (UV) absorption band observable around 277 mμ, when a flash photolysis or pulse radiolysis was applied to an aqueous solution of sodium azide, has been assumed to be due to transient azido radicals.[2,3]

Since azido radicals have been presumed to be very short-lived, we applied a radical scavenging technique by use of olefinic and nitroso compounds; our reaction system consisted of A) a solution of sodium azide, olefinic compound and nitroso compound while B) a solution of cerium (IV) salt. On mixing the two solutions we expected the formation of some stable radical intermediate containing an azido group. In the present note is reported the result of such investigations.

Experimental

The method of radical detection by ESR has already been described elsewhere.[4-6] Preliminary experiments indicated that when Ce^{4+} was mixed with only NaN_3, the evolution of N_2 was recognized by a mass filter (Shimazu, MSPEQ) probably according to the reactions:

$$Ce^{4+} + N_3^- \longrightarrow Ce^{3+} + N_3\cdot \qquad (1)$$

$$2N_3\cdot \longrightarrow 3N_2 \qquad (2)$$

On the other hand, if olefinic compounds were present in the NaN_3 solution, the generation of N_2 was more or less suppressed. The phenomena may indicate that the azido radicals formed by (1) react with olefinic

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1) Location: *Hongo, Tokyo.*
2) A. Treinin ans E. Hayon, *J. Chem. Phys.*, **50**, 538 (1969).
3) E. Hayon and N. Simic, *J. Am. Chem. Soc.*, **92**, 7486 (1970).
4) M. Setaka, Y. Kirino, T. Ozawa and T. Kwan, *J. Catalysis*, **15**, 209 (1969).
5) Y. Kirino and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **19**, 718 (1971).
6) T. Ozawa, M. Setaka and T. Kwan, *Bull. Chem. Soc. Japan*, **44**, 3473 (1971).

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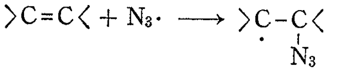
compounds probably according to



$$>C=C< + N_3\cdot \longrightarrow >\underset{\cdot}{C}-\underset{N_3}{C}< \qquad (3)$$

although the newly formed radical containing azido group was too short-lived to be detected by ESR (less than 5 msec as revealed by a rapid mixing flow technique).[7]

When Ce^{4+} was mixed with a solution containing sodium azide and both olefinic and nitroso compounds, a stable ESR spectrum was usually obtained. However, the spectral pattern in most cases appeared to be rather complex and characterized with a number of hyperfine lines depending on the kind of nitroso compound used. The use of bimolecular methyl α-nitrosoisopropyl ketone, $((CH_3)_2C(NO)COCH_3)_2$, as the scavenger, synthesized according to Aston, *et al.*[8] gave rise to a less complex spectrum. So, we shall confine ourselves to only this scavenger in the present report.

The solution A contained about 10^{-2} M NaN_3, bimolecular methyl α-nitrosoisopropyl ketone and styrene, respectively, in ethanol and B about 10^{-2} M $Ce(NO_3)_4\cdot 2NH_4NO_3$ in acetone.

We were able to observe a fairly stable ESR spectrum only when the solution A was warmed up until it became blue color characteristic of monomolecular methyl α-nitrosoisopropyl ketone[8] and thereafter brought into contact with the solution B. The blue color disappeared on mixing. The colorless solution was then evaporated to dryness and extracted wtih a mixture of acetone and benzene. The extract was then subjected to ESR measurements at room temperature.

Result and Discussion

A typical ESR spectrum obtained from the extract is illustrated in Fig. 1. It appeared however that the spectral shape was not stable enough; after left standing for a few hours at room temperature it turned out to be merely a triplet as pointed out by the three arrows at the resonance lines. Since this triplet spectrum was found to appear also for the warmed ethanol solution containing only methyl α-nitrosoisopropyl ketone, the initially observed spectrum (Fig. 1) should be regarded as superposed or due to partly a decomposed product of monomolecular methyl α-nitrosoisopropyl ketone.[9]

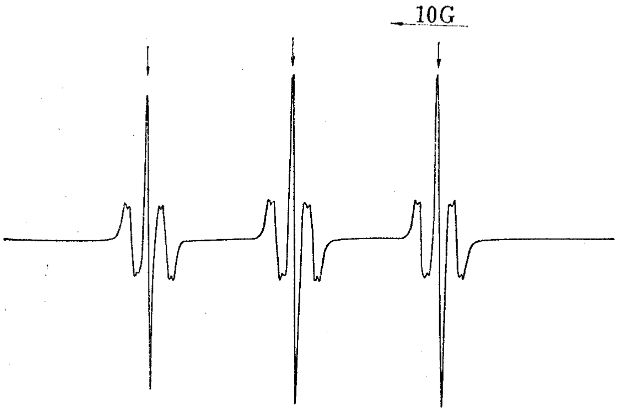
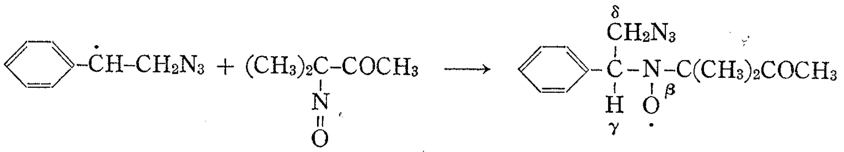


Fig. 1. ESR Spectrum for Nitroso Radical Species Containing Azido Group

We should consider now that the remaining part of the spectrum, namely, a triplet-doublet-triplet signal is due to some intermediate radical species formed during the reaction of solutions A and B. We suggest in the light of the hyperfine structure that the radical species containing azido group were formed as a result of the reaction:



(4)

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[7] The reaction products of Ce^{4+} with NaN_3 containing allyl alcohol showed a strong infrared (IR) absorption band around 2200 cm⁻¹ characteristic of organic azido compounds.

[8] J.G. Atson, D.F. Menard and M.G. Mayberry, *J. Am. Chem. Soc.*, **54**, 1530 (1932).

[9] The origin of the triplet signal would probably be ascribable to some radical intermediates formed by the partial decomposition of monomolecular nitroso compound, although we were unable to identify this radical species with certainty.

in addition to (1), (2) and (3). The hyperfine coupling constants were derived from the spectrum as:

$$A_N = 14.2G \qquad A_{H\gamma} = 3.4G \qquad A_{H\delta} = 0.4G$$

The reliability of our interpretation is still under investigations in comparison with the hyperifine coupling constants derived from the other radical intermediates containing azido group.

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Reaction of Amide Homologs. XXVI.[1] On the Products obtained from the Reaction of N-Alkylphenylacetamides with Phosphoryl Chloride

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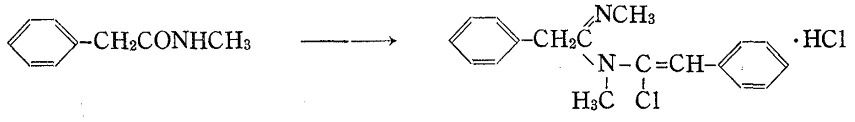
The reaction of N-ethylphenylacetamide with phosphorus pentachloride has been reported in 1932 by Heymons[3] to give N,N′-diethyl-N-(β-chlorostyryl)phenylacetamidine as the chloroplatinate. Analogous N,N′-dimethyl-N-(β-chlorostyryl)phenylacetamidine was obtained as a hydrochloride (I) in 36% yield by a reaction of N-methylphenylacetamide with phosphoryl chloride.



I

Lack of data of this compound prompts us to study the physical and chemical properties. The hydrochloride was isolated as prisms, mp 174°. Its nuclear magnetic resonance (NMR) spectrum was interpreted to fit the structure by the following assignments: the doublet at τ 6.75 to the CH_3N, the singlet at τ 6.18 to the $CH_3N=$, the singlet at τ 5.76 to the $-CH_2-$, and the singlet at τ 3.22 to the CH=. The structure was also reasonably interpreted from its infrared (IR) spectrum.

The free base could not be isolated because of its instability. However, without isolation of the free base addition of ammonia to a solution of the hydrochloride in chloroform followed by treatment with hydrogen bromide and hydrogen iodide gave the hydrobromide, mp 175° (decomp.), and the hydroiodide, mp 146—147° (decomp.), respectively, indicating the presence of one ionic chlorine atom different from the other in the hydrochloride. The hydrochloride in ethanol suffered catalytic hydrogenation over palladium-on-charcoal at ordinary pressure and temperature resulting in up-take of two molar equiv. of hydrogen. The product

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[1] Part XXV: M. Sekiya and Y. Terao, *Chem. Pharm. Bull.* (Tokyo), **19**, 391 (1971).

[2] Location: *2-2-1, Oshika, Shizuoka.*

[3] Albrecht Heymons, *Chem. Ber.*, **65**, 320 (1932).