ports[12] on the cyclization among substituent phenyl groups of the aromatic ring are published.

But it is interesting that the photocyclization among phenyl groups on the ring of N-heterocycles, as in the case of the present experiment, are scarcely known. So the present work must be very useful for the application of the syntheses of azaarens. Further investigations are now under way.

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Reactions of β-Keto Sulfide and Sulfoxide with Nitrene and Diazonium Salt

The introduction of nitrogen function to the α-carbon of sulfide *via* ylide intermediate is a versatile synthetic method. In the total synthesis of cephalosporin-C, Woodward *et al.*[1] have reported the reaction of dimethyl azodicarboxylate with (L)-(—)methyl N-*tert*-butyloxycarbonyl-2,2-dimethyl-thiazolidine-4-carboxylate to give hydrazodiester in high yield.

From this point of view, we investigated the reactivity of nitrene and diazonium compound to sulfide and sulfoxide. Here we wish to report our results of the reactions of ω-(methylmercapto)acetophenone (I) and ω-(methylsulfinyl)acetophenone (VII) with carboethoxynitrene and *p*-nitrobenzenediazonium fluoroborate.

Irradiation of I in the presence of one equivalent of ethyl azidoformate[2] in methylene chloride with a low-pressure mercury lamp for 4 hr afforded acetophenone as a sole product.[3]

On the other hand, heating of a solution of I and ethyl azidoformate in methylene bromide at 110° for 45 hr afforded 2,5-diphenyl-3,4-dimercaptomethylfurane (III) in 20% yield. mp 87°. IR $^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 1602. UV $\lambda^{\text{ethanol}}_{\text{max}}$ nm (ε): 229 (18800), 278 (13700), 320 (20800). NMR[4] δ: *ca.* 7.40 (6H, m), *ca.* 8.20 (4H, m), 2.43 (6H, s, CH_3S-). M$^+$ 330 ($C_{18}H_{16}S_2O$).[5]

However, when the reaction was run without the solvent, 1,4-diketone (IV) was obtained. mp 207°. IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 1666 (C=O). UV $\lambda^{\text{ethanol}}_{\text{max}}$ nm: 246. NMR δ: *ca.* 7.60 (6H, m), *ca.* 8.10 (4H, m) 4.97 (2H, s), 2.03 (6H, s, CH_3S-). M$^+$ 330 ($C_{18}H_{18}S_2O_2$). Diketone (IV) was converted to the furane (III) on treatment with BF_3-etherate in low yield.

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[4] The NMR spectra were taken in $CDCl_3$ solution and calibrated to internal standard of tetramethylsilane. Chemical shifts are expressed in ppm (δ): s: singlet; d: doublet; q: quartet; sept: septet; m: multiplet.

[5] Satisfactory analyses were obtained on all compounds obtained.

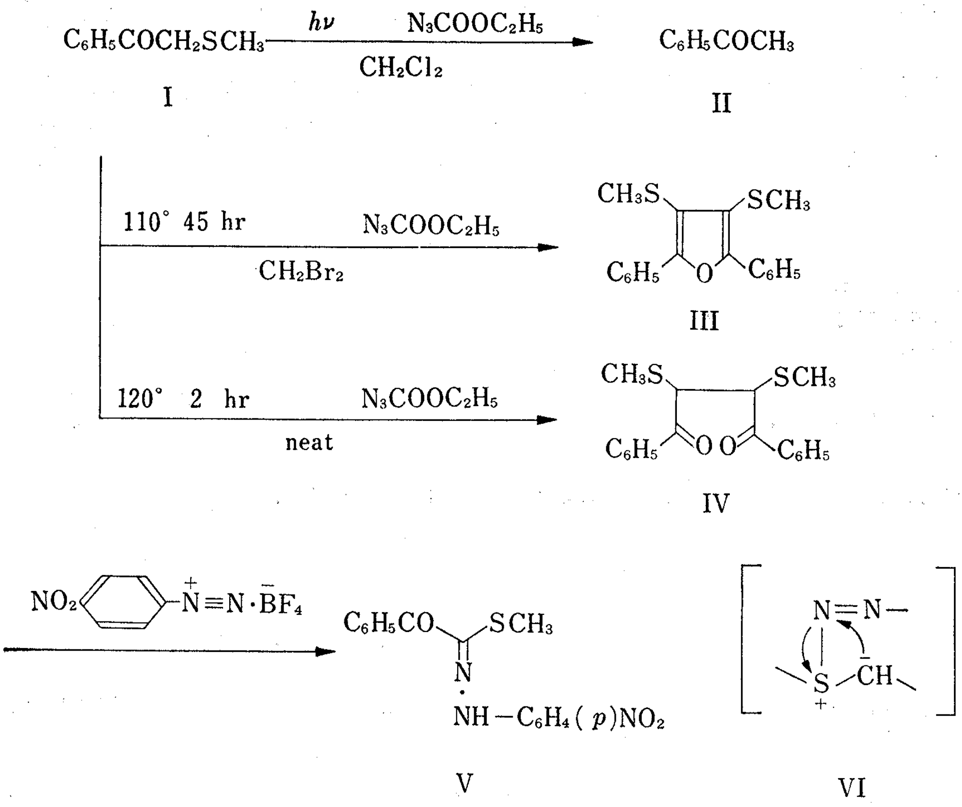

Chart 1

Dimerization of the phenacyl radical, which was generated by abstraction of hydrogen from I by carboethoxy nitrene,[6] should be responsible for the formation of IV.

Next we turned our attention to the reaction of I with diazonium salt. A solution of I and *p*-nitrobenzenediazonium fluoroborate in isopropanol was heated at 90° for one hour to afford a *p*-nitrophenylhydrazone derivative (V) in 70% yield. mp 137°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3220, 1643, 1592. UV $\lambda_{\max}^{\text{ethanol}}$ nm (ε): 255 (12800), 392 (30000). NMR δ: 9.30 (1H, br. s), 8.32—7.28 (4H, A_2B_2 almost q), *ca.* 7.60 (3H, m), *ca.* 8.0 (2H, m), 2.53 (3H, CH_3S-). M^+ 315 ($C_{15}H_{13}O_3N_3S$).

The coupling reaction between diazonium salt and active methylene compounds are well known,[7] but in our case whether the mechanism of the formation of V is the same as that of active methylene or *via* S-ylide intermediate such as VI is not obvious.

ω-(Methylsulfinyl) acetophenone (VII)[8] (4.55 g), which was easily prepared from ethylbenzoate and methylsulfinyl carbanion, was treated with *p*-nitrobenzenediazonium fluoroborate (6.0 g) under the same conditions of forming V. Four products (VIII, IX, X and XI. Yield, 660mg, 1 g, 1.5 g and 200 mg respectively) were isolated and their structures were determined to be *p*-nitrobenzenediazo methylsulfide (VIII), phenylglyoxal diisopropylacetal (IX), phenylglyoxal methylmercapto isopropylacetal (X) and phenylglyoxal dimethylmercaptal (XI) by the following physico-chemical data.

Product VIII. mp 107°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1605, 1588, 1340. UV $\lambda_{\max}^{\text{ethanol}}$ nm: 258 and 337. NMR δ: 7.78—8.41 (4H, A_2B_2 almost q), 2.93 (CH_3S-). Mass Spectrum: 197 (M^+, C_7H_7-SO_2N_3), 122 ($NO_2C_6H_4^+$), 150 (M^+- CH_3S), 75 (M^+-$C_6H_4NO_2$).

Product IX. IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1690, 1600. UV $\lambda_{\max}^{\text{Nujol}}$ nm: 245.5. NMR δ: *ca.* 8.20 (2H, m), *ca.* 7.45 (3H, m), 5.16 (1H, s), 3.94 (2H, sept, $J=6$ Hz), 1.24 (3H, d, $J=6$ Hz), 1.14 (3H d, $J=6$ Hz). Mass Spectrum: 236 (M^+, $C_{14}H_{20}O_3$).

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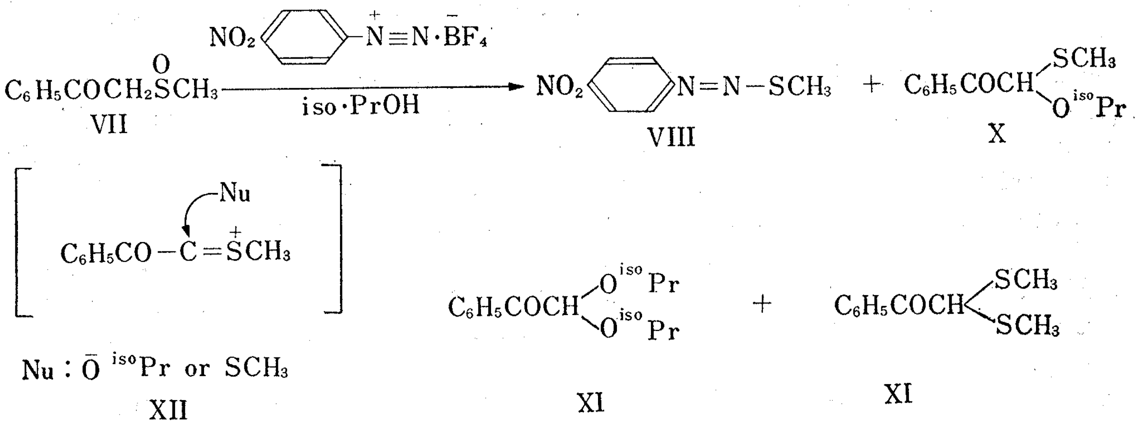

Chart 2

Product X. mp 88°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1675, 1090. UV $\lambda_{\max}^{\text{ethanol}}$ nm: 246. NMR δ: *ca.* 8.0 (2H, m), *ca.* 7.50 (3H, m), 5.77 (1H, s), 4.12 (1H, sept, J=6 Hz), 2.20 (CH_3S-), 1.22 (3H, d, J=6 Hz), 1.32 (3H, d, J=6 Hz). Mass spectrum: 224 (M^+, $C_{12}H_{16}O_2S$).

Product XI. mp 65° (lit. 66—67°).[9] IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1675. UV $\lambda_{\max}^{\text{ethanol}}$ nm: 246. NMR δ: *ca.* 8.0 (2H, m), *ca.* 7.55 (3H, m), 5.30 (1H, s), 2.15 (6H, $CH_3S \times 2$).

These products (IX, X and XI) would be formed by an intermediate of Pummerer type such as XII,[10] and product VIII would be originated from the diazonium salt and methylmercaptan from XII.

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A Novel Method for the Determination of Chinoform

Recently, Tamura and his co-workers[1] have shown the presence of 5-chloro-7-iodo-8-quinolinol (chinoform)[2] in the feces and urine of SMON patients. In the course of the investigation on the binding of chemical substances with proteins,[3] we have been interested in the complexation of this quinoline derivative with serum proteins and prompted to establish a sensitive method for its assay. This compound bears a marked structural resembrance to 8-hydroxyquinoline (oxine). The intense fluorescence of metal oxinates has been utilized in their thin-layer chromatography by Takitani and his associates.[4] This paper describes

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