In the reaction of Eq. (2), I is excited by visible light. The excited I(I*) partly plays a role of a sensitizer in Eq. (3), while it is reversely deactivated as shown in Eq. (2). The former change, Eq. (3), should be the rate-determining step. In Eq. (4), benzenesulfonylnitrene (III) must be produced besides the liberation of bromine. III is so obviously labile that it probably reacts with something, II for expamle, in the reaction system and affordes an unknown semistable substance(X), Eq. (5).

Thus, the overall rate may be expressed as

$$\frac{d[\mathrm{Br_2}]}{dt}=k_4\cdot[\mathrm{II}^*][\mathrm{I}] \qquad (6)$$

If the usual steady state treatments are made for [II*] on assuming $k_4 \gg k_3$, the equations to be used in calculation may be as follows:

$$\frac{d[\mathrm{II}^*]}{dt}=k_3\cdot[\mathrm{II}][\mathrm{I}^*]-k_4\cdot[\mathrm{II}^*][\mathrm{I}]=0 \qquad (7)$$

In addition, the presumption that the step (2) is in a partial equilibrium under the condition of ΦIa, $k_2' \gg k_3$ rationalizes Eq. (8).

$$\frac{d[\mathrm{I}^*]}{dt}=\Phi Ia-k_2'\cdot[\mathrm{I}^*]=0 \qquad (8)$$

From the Eq. (6), (7) and (8), the following rate law (9) can be derived. It fairly agreed with the experimental rate law (1).

$$\frac{d[\mathrm{Br_2}]}{dt}=\frac{k_3\cdot\Phi Ia}{k_2'}\cdot[\mathrm{II}] \qquad (9)$$

The remaining problems such as the evidence of nitrene formation, the entity of X, and the following steps to final products will be reported later.

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Studies on Peptides. Warning for the Explosive Carbazide Formation during the Direct Preparation of *t*-Butyl Azidoformate or *p*-Methoxybenzyl Azidoformate

Recently we described the direct route to prepare *t*-butyl azidoformate[1] and *p*-methoxybenzyl azidoformate,[2] which involved the introduction of phosgen to alcohols to form chloroformates followed by addition of sodium azide or hydrazoic acid in the presence of pyridine. In these experiments, the excess phosgen was removed by passing nitrogen gas into the reaction mixture prior to the addition of the azide compound.

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[1] H. Yajima and H. Kawatani, *Chem. Pharm. Bull.* (Tokyo), **16**, 182 (1968)

[2] H. Yajima and Y. Kiso, *Chem Pharm. Bull.* (Tokyo), **17**, 1962 (1969).

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We wish to make warning that if the removing step of phosgen was eliminated or was incomplete, the remaining phosgen may have a chance to react with the azide compound and to form explosive carbazide, $CO(N_3)_2$. Crystalline carbazide, prepared from carbohydrazide by the action of sodium nitrite, was described to explode vigorously by light or shaking.[3]

When *t*-butyl azidoformate was prepared by adding *t*-butanol and pyridine into an ether solution of phosgen followed by addition of the azide compound without introduction of nitrogen gas, one batch of the distillate corresponding to *t*-butyl azidoformate (bp 34—39°/35 mmHg, slightly lower than the literature value,[4] bp 73—74°/70 mmHg) exploded, even though it was stored in a freezer (−20°). It seems probable that the formation of carbazide is one of the reason responsible for this explosion.

As stated previously,[2] an unidentified by-product was detected when large excess phosgen was employed for the preparation of *p*-methoxybenzyl azidoformate (IR: -CO- 1727 cm^{-1}). It exhibited the carbonyl absorption in infrared (IR) at 1700 cm^{-1}. The same absorption band, 1700 cm^{-1} was detected in a solution of sodium azide after introduction of phosgen (IR: -CO- 1810 cm^{-1}). Appearance of this IR absorption is supposed to be an indication of carbazide formation. When this absorption is observed, the reaction mixture should be discarded.

t-Butyl azidoformate is described to be distilled quite safely under reduced pressure without carbonization,[4,5] but an instance was noted that an explosion took place in the receiving flask while this compound was being distilled under reduced pressure.[4] The reason for this explosion was unknown. With this connection, the conversion reaction of azidoformate was taken into our consideration. It is known that photolysis of *t*-butyl azidoformate in *t*-butanol liberates nitrogen gas and affords, through a nitrene intermediate, a mixture of crystalline compounds, N-*t*-butoxy-*t*-butyl carbamate and 5,5-dimethyl-2-oxazolidone.[6,7] When we condensed the ether solution of the above stated *t*-butyl azidoformate under water aspirator pressure (bath temp. 17°), some evolution of gas was noted prior to its distillation and the residue of the distillation afforded the crystalline compound. Main substance of which (IR: -CO- 1720 cm^{-1}) was found to be N-*t*-butoxy-*t*-butyl carbamate by mass spectrometric analysis, $M^+ = m/e$ 189 (D_2O treated sample, $M^+ = m/e$ 190). The molecular ion of 5,5-dimethyl-2-oxazolidone could not be detected. It seems probable that contaminated peroxide in ether employed gave such a conversion product of *t*-butyl azidoformate resemble to photolysis. It may be possible to assume that such unexpected side reaction participated also in an explosion of our distillate mentioned above.

In any case, ether free from peroxide and ethanol should be employed for the preparation of azidoformates. The latter contaminant may be converted to shock sensitive ethyl azidoformate.[8] Considering various factors involved in the preparation, it is highly preferable not to distill *t*-butyl azidoformate and to use the crude material after removal of solvents.

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