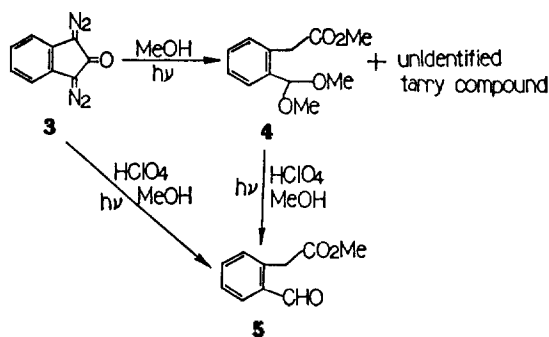


In the formation of compound 4, it seems likely that the first diazo group of compound 3 is photolyzed to carbene(6) followed by ring contraction, *i.e.* Wolff rearrangement, to give diazoketene(7). Compound 8 arises by addition of methanol to the Wolff rearranged product 7. And then compound 10 is formed from the elimination of the second diazo group remained in compound 8 by attacking of methanol.

It is generally accepted that singlet carbene generated by photolysis of diazo compounds in alcohol inserts into O-H bond rather than the C-H bond of alcohol<sup>10</sup>. Continuous irradiation of compound 10 in methanol gives to ring opened compound 4. Photolysis of compound 3 in the presence of perchloric acid (10 mol% of compound 3) for 5 hr gave *o*-(formyl) methyl phenyl acetate (16%) ( $R_f = 0.44$ , 50 % ether in hexane).



Conversion of compound 4 into compound 5 was carried out under the same condition for 2 hr. We have obtained compound 5 (53%) as a major product by the TLC.

The formation of compound 5 was probably due to acid hydrolysis of compound 4. The 2,4-dinitrophenylhydrazone of compound 5 was formed as red crystals, which melted at 232-234 °C (decomp).

We think that both photolytic reactions of compound 3

proceed in same pathways.

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11. Spectroscopic data (<sup>1</sup>H-NMR, IR, GC-MS) were obtained for the compounds: 1,3-bis(oximino)-2-indanone(2); mp 225-226 °C; IR(KBr) 3000-3400, 1740, 1420, 1005, 840 cm<sup>-1</sup>; 1,3-bis(diazo)-2-indanone(3); mp. 126-127 °C; <sup>1</sup>H-NMR (60 MHz, CCl<sub>4</sub>) δ 7.2(s, 4H); IR(KBr) 2100, 1650, 1360, 1180 cm<sup>-1</sup>; *o*-(dimethoxy methyl)methyl phenyl acetate(4); <sup>1</sup>H-NMR (60 MHz, CCl<sub>4</sub>) δ 7.1-7.5(m, 4H, Ar-H), 5.4(s, 1H, CH), 3.68(s, 2H, CH<sub>2</sub>) 3.62(s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.2(s, 6H, 2OCH<sub>3</sub>); IR(NaCl) 1740, 1430, 1340, 1150, 1050 cm<sup>-1</sup>; GC-MS *m/e* 224(M<sup>+</sup>) 161(B): *o*-(formyl) methyl phenyl acetate(5); <sup>1</sup>H-NMR (60 MHz, CCl<sub>4</sub>) δ 10(s, 1H, CHO), 7.1-7.8(m, 4H, Ar-H), 3.9(s, 2H, CH<sub>2</sub>), 3.5(s, 3H, CO<sub>2</sub>CH<sub>3</sub>); IR(NaCl) 1740, 1705, 1250, 1160 cm<sup>-1</sup>.

## Photochemistry of 1,3-Bis(diazo)-2-indanone in Argon Matrix at Low Temperature

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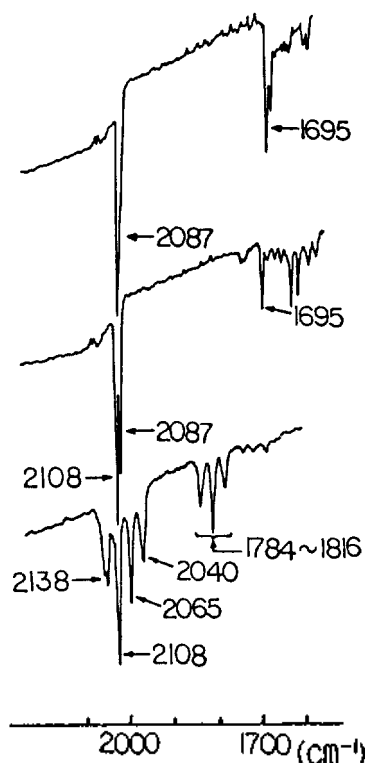
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Ring contraction of bis(diazo)keto compounds represents a general method for the preparation of highly strained ring compounds<sup>1</sup>. Attempts to generate cycloheptyne<sup>2</sup>, cyclohexyne<sup>3</sup> and cyclopentyne<sup>4</sup> have been successful with corresponding diazo compounds. But the synthesis of the more

strained cyclic alkyne, such as cyclobutyne has been unsuccessful. The mechanism of the photochemical Wolff rearrangement adds special interest to the ring contraction of bis(diazo)keto compounds<sup>5</sup>. Stereochemical<sup>6</sup> and CIDNP<sup>7</sup> evidence is consistent, in most cases of Wolff rearrange-



**Figure 1.** Characteristic IR spectrum (2200  $\text{cm}^{-1}$ -1600  $\text{cm}^{-1}$ ) of overall experiments in argon matrix. Before irradiation of 1,3-bis(diazo)-2-indanone (upper). After irradiation ( $\lambda > 350$  nm) for 20 sec (middle). After irradiation ( $\lambda > 270$  nm) for 42 min (lower).

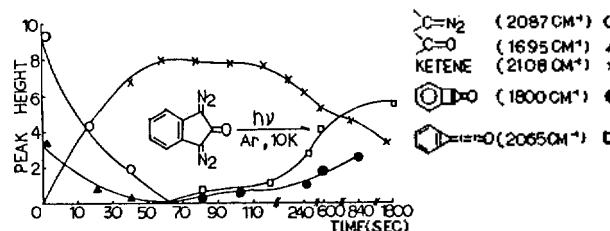
ment, with concerted loss of nitrogen and migration of the carbon-carbon bond<sup>8</sup>.

In this communication, we report the photochemical reaction of 1,3-bis(diazo)-2-indanone in argon matrix. The photoproducts were observed by infrared spectrometer. 1,3-Bis(diazo)-2-indanone(1) was synthesized from 2-indanone using Foster reaction.<sup>9</sup> Compound 1 was sublimed onto the CsI cell at 10 K ( $1 \times 10^{-6}$  mmHg) and codeposited with argon. Matrix ratio(sample to argon) was maintained 1:500 using a Neupro gauge. Irradiation was carried out by high pressure 300W Hg lamp. A 10 cm path length of distilled water served as an infrared filter to minimize heating of the matrix during irradiation.

Irradiation( $\lambda > 350$  nm, Toshiba Filter D35) of 1,3-bis(diazo)-2-indanone matrix isolated in argon at 10 K gave a diazoketene by Wolff rearrangement, as confirmed by the appearance of the ketene band ( $\text{C}=\text{C}=\text{O}$ , 2108  $\text{cm}^{-1}$ ) as a primary product via an intermediate 2. Monitoring the reaction as a function of irradiation time revealed that 2108  $\text{cm}^{-1}$  ( $\text{C}=\text{C}=\text{O}$ ) band grew rapidly and 2087  $\text{cm}^{-1}$  ( $\text{C}=\text{N}_2$ ) band was decreased. The structural assignment was based on the intense infrared stretching vibration for ketene at 2108  $\text{cm}^{-1}$  and weak diazo vibration at 2087  $\text{cm}^{-1}$ . The diazo and ketone bands were disappeared within 1 min.

In 1985, Chapman reported the ring contraction of diazoketenes and interpreted the results on the basis of a nonconcerted Wolff rearrangement which proceeded through  $\alpha$ -keto-carbene intermediates.<sup>10</sup> But we could not observe keto-carbene intermediate which was expected around 1644  $\text{cm}^{-1}$ .

Continuous irradiation ( $\lambda > 350$  nm, 1 min) of compound 3 matrix isolated in argon gave compound 5 (2065  $\text{cm}^{-1}$ , 2040

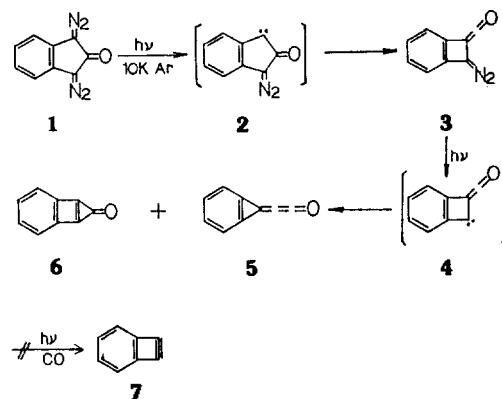


**Figure 2.** Characteristic IR bands changed on irradiation time.

$\text{cm}^{-1}$ ) and compound 6 (1784-1816  $\text{cm}^{-1}$ ). The structures of 5 and 6 were determined by IR spectra compared with previous reports<sup>4,11,12</sup>. Irradiation ( $\lambda > 270$  nm, Toshiba Filter UV 27) of compound 5 and 6 gave rise to carbon monoxide. A band of carbon monoxide which was eliminated from compound 5 and 6 was getting bigger on irradiation time.

Irradiation ( $\lambda > 350$  nm) of compound 1 in an argon/oxygen (80:20) matrix did not give Wolff rearrangement product 3 but an unidentified photoproduct was observed at 1720  $\text{cm}^{-1}$ . Attempts to degrade compound 5 and 6 ( $\lambda > 270$  nm, 15 hr) to benzocyclobutene by UV irradiation were unsuccessful although we observed carbon monoxide band by infrared spectrometer. The absorption changes of some characteristic IR bands on irradiation time were shown in Figures 1 and 2.

From this IR spectra, we propose that the primary photoproduct obtained upon irradiation of 1,3-bis(diazo)-2-indanone(1) is the diazoketene(3) which undergoes the reactions illustrated in Scheme 1. Formation of compound 3, 5 and 6



**Scheme 1**

could be viewed as a concerted reaction of carbenes. The infrared bands of compound 5 and 6 in argon matrix were disappears by warming from 10 K to 60 K.

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## An Efficient Reduction of Acid Chlorides by Sodium Borohydride with Dropwise Addition of Methanol

Suk-Ku Kang\* and Dong-Ha Lee

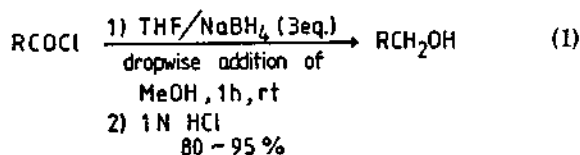
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The conversion of acid chlorides to the corresponding alcohols by reduction with sodium borohydride is of great practical interest because the conversion of acid or acid esters to the corresponding alcohols needs lithium aluminum hydride or other reducing agents which are more expensive and more difficult to handle than sodium borohydride.

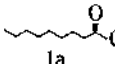
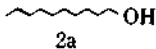
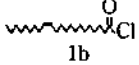
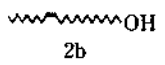


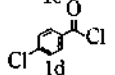
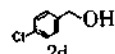










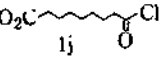
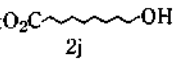
In the literature, it was reported<sup>1</sup> that aliphatic acid chlorides were reduced to the corresponding alcohols by employing a suspension of sodium borohydride in dioxane. But the results on the reductions of unsaturated and other polyfunctional acid chlorides were less clean-cut. It was also reported<sup>2</sup> that acid chlorides cannot be reduced to alcohols by sodium borohydride in the presence of hydroxylic solvent. In this paper<sup>2</sup>, the acid chlorides react with these solvents to yield products which are unreactive towards borohydride. Recently, certain aromatic acid chlorides were reduced<sup>3</sup> cleanly to the corresponding benzyl alcohols by sodium borohydride in a mixture of toluene and water in the presence of a phase-transfer catalyst.

We have found that acid chlorides could be easily and conveniently reduced into the corresponding alcohols by sodium borohydride in tetrahydrofuran with dropwise addition of methanol in good yields (Eq. 1). Acid chlorides were readily prepared from the corresponding acid by treatment of thionyl chloride.



Erucic acid chloride (**1b**) which could be readily prepared from erucic acid was conveniently reduced to the erucyl alcohol (**2b**) in 93% yield, which is an intermediate for the economical synthesis<sup>4</sup> of muscalure<sup>5</sup>, the sex pheromone of the housefly, *Musca domestica* L.. From the  $\alpha,\beta$ -unsaturated acid chloride (**1c**), the corresponding allylic alcohol (**2c**) was obtained as the only isolated product (Entry 3). The sterically hindered acyl chloride (**1i**) was also easily reduced in the alcohol (**2i**) (Entry 9). In the presence of ester group, acid chloride (**1j**) was selectively reduced into the corresponding

Table 1. Reduction of Acid Chlorides by Sodium Borohydride

Entry	Substrate <sup>a</sup>	Temp (°C)	Time(h)	Product <sup>b</sup>	Yield (%) <sup>c</sup>
1		rt	1		80
2		rt	1		93
3		rt	1		92
4		rt	1		93
5		rt	1		92
6		rt	1		94
7		rt	1		95
8		rt	1		93
9		rt	1		89
10		rt	1		92

<sup>a</sup>All the acid chlorides were prepared from the corresponding acids and thionyl chloride. <sup>b</sup>Consistent spectral data were obtained for all compounds. <sup>c</sup>The yields were not optimized and represent pure isolated yields.

alcohol (**2j**) (Entry 10).

The following procedure is representative. To 3.0 ml of dry THF solution was added erucic acid chloride (0.200g, 0.60 mmol) and the sodium borohydride (0.068g, 1.8mmol) in one portion. Methanol (1.5 ml) was added to the reaction mixture drop by drop for 1h at room temperature. Then, 1N