

REACTION OF *o*-ACYLPHENYLDIAZOMETHANE I. FORMATION OF 1-ALKOXY-
ISOBENZOFURANS BY INTRAMOLECULAR CARBENIC REACTION

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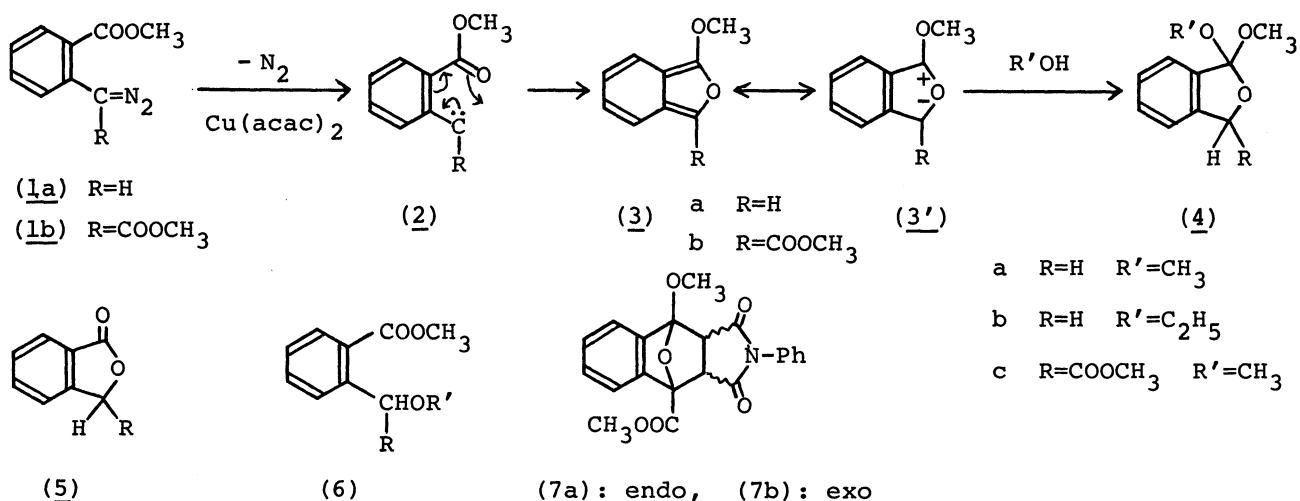
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1-Methoxyisobenzofurans were generated as the transient intermediate in the $\text{Cu}(\text{acac})_2$ catalyzed decomposition of methyl *o*-diazomethylbenzoate. The intermediates were confirmed by trapping with dienophiles or alcohols to give Diels-Alder adducts and cyclic orthobenzoates (4), respectively.

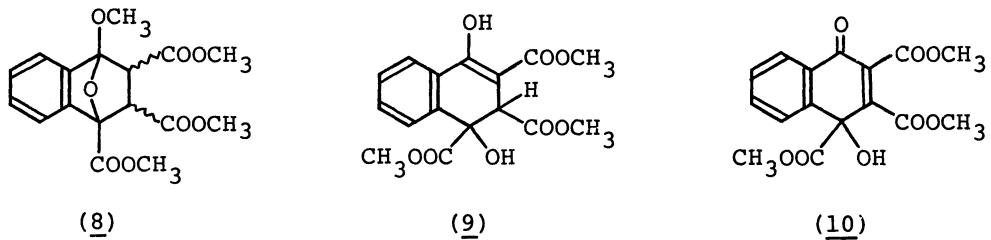
The intramolecular carbene-carbonyl reaction has been found to be the efficient method for the formation of reactive species such as carbonyl ylide,¹ because (i) starting diazo compounds are easily obtainable, and (ii) leaving group (N_2) is inert to the reactive products. There is only a few work on the formation of isobenzofuran by the decomposition of diazo compound. 1,3-Diphenylisobenzofuran was reported to be formed by the decomposition of *o*-(α -diazobenzyl)benzophenone which was generated in situ in the photochemical decomposition of 1,4-diphenylphthalazine N-oxide.² In this letter, we report the first example of the formation of 1-alkoxyisobenzofurans by carbene-carbonyl reaction.

Methyl *o*-diazomethylbenzoate (1a) was decomposed in methanol in the presence of $\text{Cu}(\text{acac})_2$ at room temperature. The reaction proceeded with vigorous evolution of nitrogen gas which ceased in a few seconds. After evaporation of the solvent, the residue was extracted with boiling n-pentane to remove the catalyst. Nmr spectrum of the pentane soluble part showed signals at 6.67 (s, 2 OCH_3), 4.78 (s, 2H), and 2.3-2.9 τ (m, 4H), and its ir spectrum showed no absorption at carbonyl region. Although the product was not isolated in a pure state, spectral data revealed it a single product, which was assigned as cyclic orthobenzoate (4a). Formation of phthalide (5) by the treatment with dil. HCl supported the structure. The decomposition of 1a in ethanol also gave 4b in almost quantitative yield.

Catalytic decomposition of diazoester (1b: R=COOCH₃) in methanol at 60°C gave similar product in quantitative yield; nmr(CDCl_3): 6.67, 6.58, 6.18 (s, 3 OCH_3), 4.30 (s, 1H), and 2.2-2.9 τ (m, 4H, Ar). In these reactions, benzyl ethers (6) which were expected from the intermolecular insertion of carbene (2) into O-H bond of alcohols were not detected. These facts suggested that the carbene (2) preferred the intramolecular attack on carbonyl oxygen to intermolecular attack on the solvent, and yielded 1-methoxyisobenzofurans (3) which reacted with alcohols to give 4. The direction of the addition of alcohols suggests the resonance contribution of carbonyl ylide(3') in 1-methoxyisobenzofurans.



In order to confirm the transient formation of 3, trapping experiment of 3 with dienophiles was performed. When the decomposition of 1b was carried out in the presence of 1.2 molar amount of N-phenylmaleimide at 80°C, Diels-Alder adducts (7a) and (7b)³ were obtained in yields of 45% each. Configuration of endo-and exo-adduct was assigned by their nmr spectra.⁴ Reaction of 3b (R=COOCH₃) with dimethyl fumarate gave adduct (8),³ mp 142-145°C, and enol (9) in yields of 15% and 83%, respectively; 9, mp 151-152°C, nmr(CDCl₃): 6.49, 6.35, 6.17 (s, 3 OCH₃), 5.80 (s, 1H); 5.40 (s, 1H), 2.0-2.7 (m, 4H), and -2.65 τ (s, OH), ir(KBr): 3420 (OH), 1735 (ester C=O), and 1645 cm⁻¹ (β-keto ester). The major product (9) seems to be yielded by hydrolysis of adduct (8) in the course of silica gel column chromatography, because the reaction mixture (before column chromatography) showed no OH absorption. The reaction of 3b with dimethyl acetylenedicarboxylate gave enone (10) in 92% yield; mp 141-142°C, nmr(CDCl₃): 6.32, 6.12, 6.08 (s, 3 OCH₃), 5.07 (broad s, 1H), and 1.7-2.7 τ (m, 4H), ir(KBr): 3400 (OH), 1750 (ester C=O) and 1660 cm⁻¹ (C=C).



References and Notes

- 1 M.Hamaguchi and T.Ibata, *Tetrahedron Lett.*, 4475 (1974) and references cited.
- 2 K.B.Tomer, N.Harrity, I.Rosenthal, O.Buchardt, P.L.Kumler, and D.Creed, *J.Amer.Chem. Soc.*, 95, 7402 (1973).
- 3 All new compounds reported herein showed satisfactory elemental analyses and Diels-Alder adducts (7a), (7b), and (8) showed satisfactory nmr and ir spectra.
- 4 Endo-adduct (7a) showed shielded signal of ortho-protons of N-phenyl group at 3.5-3.7 τ ; D.W.Jones and G.Kneen, *J.C.S.Perkin I*, 171 (1975).

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