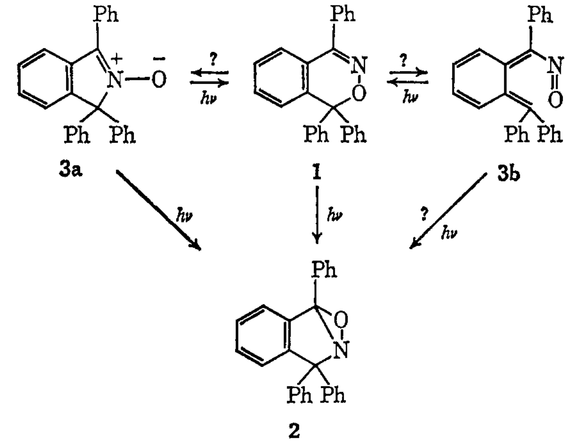
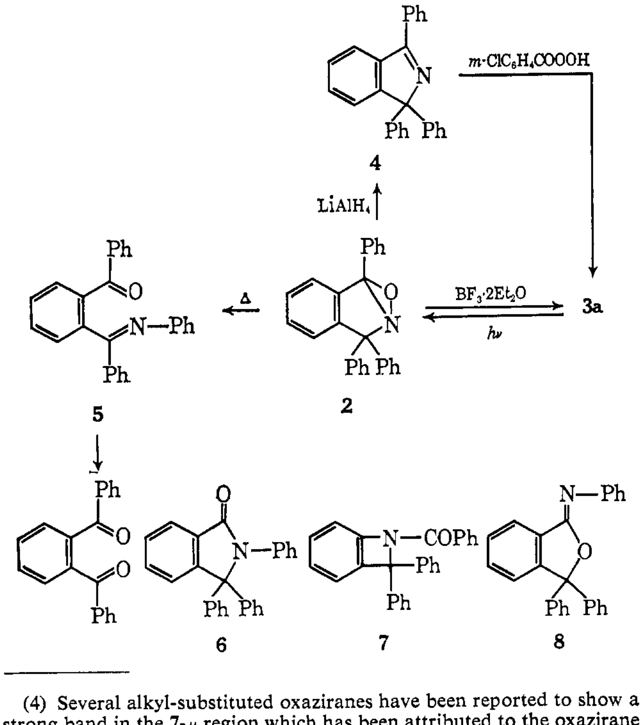


The infrared spectrum lacked the 11.0-μ band (N–O stretch due to the PhC(Ar)=NO– moiety) characteristic of the starting material and possessed a strong band at 7.49 μ, well within the range expected for an oxazirane structure.[4] The mass spectrum (71 eV) of **2** showed its parent peak at *m/e* 361, together with other major fragments at 345, 331, 285 and 77.

Reaction of **2** in benzene solution with boron trifluoride diethyl ether followed by decomposition with cold aqueous sodium bicarbonate yielded the nitrone[5,6] **3a** (87%): mp 198°; $\lambda_{max}^{CH_3CN}$ 335 (ϵ 8000), 317 (7100), 252 mμ (29,500); ir (Nujol) 6.30, 6.59, 6.95, 8.70 μ; *m/e* 361 (parent), together with other fragments at 345 and 77. Ultraviolet irradiation of **3a** transformed it quantitatively to the oxazirane **2**. The latter transformation is quite characteristic of the nitrones.[7]



As expected, reduction of **2** with LiAlH$_4$ in refluxing ether produced[5,6,8] **4** (90%): mp 145–146°; $\lambda_{max}^{CH_3CN}$ 270 (ϵ 5100), 243 mμ (11,600); ir (Nujol) 6.25, 6.42, 6.70, 6.90 μ; *m/e* (parent) 345. Further proof for structure **4** was provided by its quantitative conversion to the nitrone **3a** when treated with *m*-chloroperbenzoic acid in dry dichloromethane.[6,9]

Additional insight into the oxazirane structure **2** was provided by its nearly quantitative (91%) thermal isomerization[11] (170–180°, 0.5 hr) to the monoanil **5** of *o*-dibenzoylbenzene: mp 95–97°; $\lambda_{max}^{CH_3CN}$ 330 (ϵ 2780), 250 mμ (28,300); ir (Nujol) 6.02 (C=O), 6.19 μ (C=N);[12] *m/e* 361 (parent), 180, 103. Compelling evidence in favor of structure **5** and against possible structures **6**, **7**, or **8** was furnished by its hydrolysis (5% aqueous methanolic H$_2$SO$_4$) to *o*-dibenzoylbenzene (86%), mp 146–147°, identified by comparison with an authentic sample (melting point, mixture melting point, ir, uv).

With regard to the mechanism of the photoisomerization **1** → **2**, direct transformation of the benzoxazine **1** to the oxazirane **2** appears likely, though intervention of intermediates such as **3a** or **3b** cannot be excluded. Further studies directed toward the mechanistic details of this reaction are in progress.

Acknowledgment. I wish to thank Dr. A. Zweig for his critical comments.

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(4) Several alkyl-substituted oxaziranes have been reported to show a strong band in the 7-μ region which has been attributed to the oxazirane ring [H. Krimm, *Ber.*, **91**, 1057 (1958)]. Also 2,2,5-trimethyl-6-oxa-1-azabicyclo[3.1.0]hexene shows an infrared absorption band at 7.44 μ not present in the parent 2,5,5-trimethyl-1-pyrroline.[7d]

(5) For a summary of oxazirane reactions see E. Schmitz, *Advan. Heterocyclic Chem.*, **2**, 83 (1963).

(6) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

(7) (a) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957); (b) J. S. Splitter and M. Calvin, *ibid.*, **23**, 651 (1958); (c) R. Bonnett, V. M. Clark, and A. R. Todd, *J. Chem. Soc.*, 2102 (1959); (d) L. S. Kaminsky and M. Lamchen, *ibid.*, 2295 (1967).

(8) Treatment of **2** with potassium iodide in aqueous–ethanolic acetic acid solution produced **4** and iodine.

(9) Ordinarily most imines yield oxaziranes with peracids,[6,10] but formation of nitrone in the present case may be due to the lowered basicity of the C=N bond due to extensive substitution. The oxazirane **2** was found not to rearrange under the experimental conditions in the presence of the peracid.

(10) R. G. Pews, *J. Org. Chem.*, **32**, 1628 (1967).

(11) The failure of **2** to yield the amides **6** or **7** (or the nitrone **3a**) may be due to steric crowding (which minimizes the orbital overlap between the migrating centers) of the transition states leading to their formation.

(12) A band of comparable intensity was also observed at 6.18 μ in the infrared spectra of *o*-methylbenzophenone anil and *o*-(α-isopropylidenebenzyl)benzophenone anil and was assigned to the C=N bond in these molecules (K. R. Huffman, unpublished work).

Balwant Singh
Central Research Division, American Cyanamid Company
Stamford, Connecticut 06904

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Photolytic Isomerization of Aromatic Species. Poly-*t*-butylfurans

Sir:

Recent investigators[1-4] have observed that various five-membered aromatic heterocycles undergo specific light-induced rearrangements involving over-all transposition of annular atoms, similar to the irradiation-induced interconversions of poly(alkylbenzenes) involving valence bond isomers.[5] With a singular exception,[1] no intermediates in such processes have been isolated, identified, and studied, and the general mechanism of such photoisomerizations has remained correspondingly uncertain. By employing means which

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(1) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967).

(2) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967), and earlier papers.

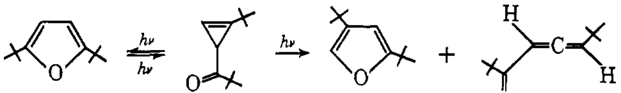
(3) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Helv. Chim. Acta*, **50**, 2244 (1967).

(4) P. Beak, J. L. Miesel, and W. R. Messer, *Tetrahedron Letters*, 5315 (1967).

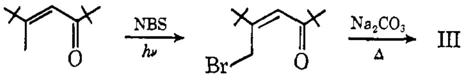
(5) For an account of the early history of this phenomenon, see E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965).

permitted the first isolation of a benzene valence bond isomer,[6] we have now succeeded in interrupting the over-all isomerization of a representative simple heterocyclic case (*i.e.*, substituted furan) and fully characterizing the isolated substance, believed to be an actual intermediate in the over-all change.

When a 1.2×10^{-3} *M* solution of 2,5-di-*t*-butylfuran (I)[7] in pentane was irradiated under nitrogen for 1 hr,[8] approximately 50% of the starting material was consumed, and there were formed three major products, isolated by glpc and shown to be cyclopropenyl ketone II (4%), 2,4-di-*t*-butylfuran (III) (9%), and allenyl ketone IV (9%).[9] The remainder of the material was accounted for by much less volatile products, presumably dimers and higher oligomers. Mass spectrometry showed that all three compounds were isomeric with the starting furan. Ketone II ($\nu_{C=O}$ 1690 cm^{-1}, $\nu_{C=C}$ 1790 and 1773 cm^{-1}) displayed in the nmr spectrum *t*-butyl singlets at τ 8.88 and 8.82 and doublets at τ 7.33 and 4.09 (J = 1.5 Hz), all in the expected ratio. Allene IV ($\nu_{C=C=C}$ 1951 cm^{-1}, $\nu_{C=O}$ 1680 and 1667 cm^{-1}) revealed strong uv absorption [λ_{max}^{EtOH} 228 mμ (ϵ 6660)] and nmr resonances for two *t*-butyl groups (τ 8.88 and 8.84) and two olefinic protons on different carbons (τ 4.45 and 3.98, doublets, J = 6.2 Hz).[10] The identity of furan III was established by comparison with an authentic sample prepared by route A.[11]



I II III IV

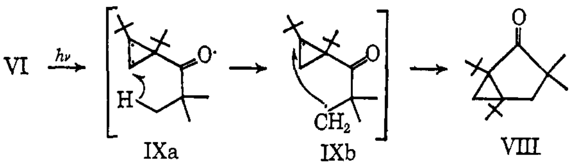


(A)

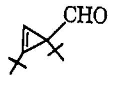
That the cyclopropenyl ketone indeed acts as an intermediate in the conversion of starting furan to products was indicated by the fact that the ratios III/II and IV/II both increase continuously over irradiation for 170 min and extrapolate to 0 at 4 min, about the time required for the radiation source to produce useful light in the region absorbed by I. This observation is consistent only with an initial rate of formation of products III and IV of zero. The central role of II was further demonstrated by irradiation[8] of a 3.7×10^{-3} *M* solution in pentane: in 10 min, the cyclopropene had been transformed (84% reaction) into a mixture of I (9%), III (14%), and IV (23%). No appreciable quantities of any of these products could have been formed by secondary photolysis of I.

Irradiation of the isomeric furan III under similar conditions led to the formation of the cyclopropenealdehyde V[12] as the only isolable product, in addition to a large amount of nonvolatile material. No trace of I, II, III, or IV was formed under these conditions.

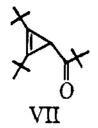
The irradiation of the highly congested 2,3,5-tri-*t*-butylfuran (VI)[13] gives the cyclopropenyl ketone VII[12] in small yield (~5%). However, the most abundant photoproduct (~95%) is the result of a novel and unexpected rearrangement, presumably again involving an intermediary cyclopropenyl ketone. It was isolated by glpc as a colorless oil (M$^+$ 236) with ir and uv spectra indicative of the presence of a ketone conjugated with a cyclopropyl group [ν_{max} 3060 and 1719 cm^{-1}, λ_{max}^{EtOH} 206.5 (ϵ 6540) and 291 mμ (143)].[10] The nmr spectrum confirmed the cyclopropyl methylene (τ 9.39, doublet, 1 H, J = 5.5 Hz; and 8.61, doublet of doublets, 1 H, J = 5.5 Hz, J' = 1.9 Hz) and revealed that only two *t*-butyl groups remained in the molecule [singlets at τ 8.88 (9 H) and 8.82 (9 H)]. In addition, there were present a pair of magnetically equivalent methyl groups (singlet, τ 9.00, 6 H) and a further pair of protons forming an ABX system (τ 8.0 and 8.3, J_{AB} = 8.4 Hz), with the low-field member of this pair further split by coupling (J' = 1.9 Hz) with the lower field cyclopropyl proton. The tentative assignment VIII permitted by these data was confirmed by (i) LiAlH$_4$ reduction to the corresponding secondary alcohol, (ii) Li–NH$_3$ reduction to 3,5,5-trimethyl-2,3-di-*t*-butylcyclopentanone, and (iii) perchloric acid catalyzed rearrangement to 2,4-di-*t*-butyl-6,6-dimethylcyclohex-2-enone, which was identical with material obtained by alternate synthesis involving bromination–dehydrobromination of the corresponding cyclohexanone.[14] The formation of the bicyclo[3.1.0]hexanone VIII from 2,3,5-tri-*t*-butylfuran may involve internal hydrogen transfer from the *t*-butyl ketone unit to the excited olefinic center in the cyclopropenyl ketone (IXa), followed by bonding of the two resulting radical centers (IXb).[15]



IXa IXb VIII



V



VII

The above findings suggest that the Δ^2-cyclopropenyl ketone type be designated as a true intermediate in the photoinduced interconversion of alkyl-substituted furans and intimate that similar cyclopropenyl types act similarly in allied heterocyclic systems. This conclusion accords with (i) the finding of Ullman and Singh that rearrangement of 3,5-diphenylisoxazole to 2,5-diphenyloxazole is mediated by an azirine,[1,16] (ii) the observations by Srinivasan of the vapor-phase decom-

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[6] E. E. van Tamelen, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

[7] For preparation, see A. Ramasseul and A. Rassat, *Bull. Soc. Chim. France*, 2214 (1963).

[8] Hanovia 450-W medium-pressure mercury arc with Vycor filter (λ >2200 Å). All yields are corrected for recovered starting material.

[9] Previous work on the photolysis of simple furans has been concerned with vapor-phase behavior, the principal over-all pathway being extrusion of carbon monoxide and formation of cyclopropenes [R. Srinivasan, *J. Am Chem. Soc.*, **89**, 1758 (1967); **89**, 4812 (1967)].

[10] Ir and nmr spectra measured on substances in carbon tetrachloride or deuteriochloroform solutions.

[11] This furan has been prepared by another route: J. A. Miller, M. H. Durand, and J. E. Dubois, *Tetrahedron Letters*, 2831 (1965).

[12] Structural assignment based on ir, nmr, and mass spectral data.

[13] H. Wynberg and U. E. Wiersum, *Chem. Commun.*, 1 (1965).

[14] Prepared by the methylation of 2,4-di-*t*-butyl-6-methylcyclohexanone [A. C. Whitaker, *J. Am. Chem. Soc.*, **69**, 2415 (1947)].

[15] Photochemical reduction of the double bond in β,γ-unsaturated ketones has been observed [R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966)].

[16] The findings reported herein demonstrate that the formation of cyclopropenyl intermediates is not confined to systems which feature a weak bond, as the nitrogen–oxygen link in the pioneering case of Ullman and Singh.[1]

position of furan itself,[17] and (iii) the opinions of Schmid regarding pyrazole and indazole photolyses.[1]

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(17) Srinivasan[9] also isolated in the parent furan case an adduct believed to be derived from Δ^2-cyclopropenaldehyde (i) and furan, while an unstable "dimethyl derivative corresponding to the aldehyde (i)," but of otherwise unspecified structure, was detected as a product from 2,5-dimethylfuran.

(18) NSF Graduate Fellow, 1963–present.

E. E. van Tamalen, Thomas H. Whitesides[18]
Department of Chemistry, Stanford University
Stanford, California 94305
Received March 1, 1968

A Carbon Dioxide Insertion Reaction into the Co–H Bond of Nitrogentris(triphenylphosphine)cobalt Hydride

Sir:

The discovery of the reaction of a tris(triphenylphosphine)cobalt complex with molecular nitrogen under mild conditions[1–3] led us to examine the reactions of the complex with other "inert" gases including carbon dioxide. The insertion reactions of CO_2 into metal–carbon bonds of organo non-transition metal compounds are well known, but very few reports have been made on the reaction of CO_2 with transition metal compounds. Recently reactions of CO_2 with platinum and palladium complexes[4,5] were reported, but the reactions require the presence of oxygen, and carbonato complexes were formed. We wish to report here a novel insertion reaction of CO_2 into a cobalt–hydride bond.

When a CO_2 stream was bubbled through a benzene or tetrahydrofuran solution of $H(N_2)Co[P(C_6H_5)_3]_3$[6] (**1**) containing triphenylphosphine at room temperature, the original red color changed to brownish green with a loss of molecular nitrogen from the complex, as proved by mass spectroscopy. On concentration of the solution, green crystals were obtained which were repeatedly washed with diethyl ether and dried *in vacuo;* mp 217–220° dec; yield about 45% as $HCOOCo[P(C_6H_5)_3]_3$ (**3**). *Anal.* Calcd for $C_{55}H_{46}O_2P_3Co$: C, 74.2; H, 5.2. Found: C, 73.6; H, 5.2. The same complex was obtained in a similar manner by the reaction of $H_3Co[P(C_6H_5)_3]_3$[6] (**2**) with CO_2. This complex is soluble in aromatic hydrocarbons or tetrahydrofuran, but attempts to recrystallize the complex in these solvents always resulted in partial decomposition of the complex. Presumably the complex dissociates in solution accompanied by irreversible decomposition.

The green crystals **3** were characterized as a formate complex of cobalt on the following basis. The infrared spectrum of the complex indicates two strong bands at 1620 and 1300 cm^{-1} which can be assigned to antisymmetric and symmetric stretching vibrations of a $HCOO^-$ group attached to cobalt. The treatment of the green complex with concentrated sulfuric acid released 1 mol of CO and 0.5 mol of H_2 per mol of the cobalt complex. Thermal decomposition of the complex *in vacuo* at 200–250° liberated CO_2 with a small amount of CO and H_2, as proved by mass spectrometry. The amount of CO_2 and CO evolved corresponded to about 0.85 mol/Co. The reaction of **3** with methyl bromide led to the formation of methyl formate which was identified by infrared spectroscopy after the separation of the ester from the reaction mixture by preparative gas chromatography. The reaction of **3** with dry hydrogen chloride gas at 20° gave HCOOH, as proved by infrared spectroscopy.

The formation of the formate complex **3** by the reaction of cobalt hydrides **1** and **2** with CO_2 can be interpreted as the insertion of CO_2 into the cobalt–hydride bond.

$$\underset{\mathbf{1}}{H(N_2)Co[P(C_6H_5)_3]_3} + CO_2 \longrightarrow \underset{\mathbf{3}}{HCOOCo[P(C_6H_5)_3]_3} + N_2$$

This reaction provides, to our knowledge, the first example of CO_2 insertion among transition metal complexes.

The formate complex **3** can also be prepared by the reaction of **1** with formic acid in a yield of about 65%. In this case the evolution of nitrogen and hydrogen in a molar ratio of about 1:1 was observed. The melting point and the infrared spectrum of the complex obtained by this reaction were identical with those of the complex **3** prepared by the reaction of **1** or **2** with CO_2.

$$H(N_2)Co[P(C_6H_5)_3]_3 + HCOOH \longrightarrow HCO_2Co[P(C_6H_5)_3]_3 + N_2 + H_2$$

When the reaction of **1** with CO_2 was carried out in the absence of tripenylphosphine, a small amount of yellow crystals was obtained. The complex can be formulated as $\{Co(CO[P(C_6H_5)_3]_3\}_x$ (**4**) (probably $x = 2$), mp 158–160° dec. *Anal.* Calcd for $C_{55}H_{45}OP_3Co$: C, 75.6; H, 5.2. Found: C, 75.3; H, 5.8. Iodolysis and pyrolysis of **4** released 1 mol of CO/mol of cobalt complex, and the evolution of hydrogen was not detected by mass spectroscopy.

The same product was also prepared by the reaction of **1** with benzyl isocyanate. The infrared spectrum of complex **4** shows a strong band at 1877 cm^{-1} which may be assigned to the CO stretch of bridged cobalt carbonyl groups as compared with the CO stretch at 1915 cm^{-1} of $H(CO)[P(C_6H_5)_3]_3$ which was prepared by the reaction of **1** with carbon monoxide.[7]

The insertion reaction of CO_2 into a cobalt–carbon bond is now under investigation and will be reported later.

Acknowledgment. The authors are grateful for the experimental assistance of Mr. Y. Kubo.

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(1) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

(2) A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967); A. Misono, Y.Uchida, T. Saito, and K. M. Song, *Chem. Commun.*, 419 (1967).

(3) A. Sacco and M. Rossi, *ibid.*, 316 (1967).

(4) C. J. Nyman, C. E. Wymore, and G. Wilkinson, *ibid.*, 407 (1967); F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *ibid.*, 408 (1967).

(5) S. Takahashi and N. Hagihara, presented at the 19th Annual Meeting of Chemical Society, Tokyo, Japan, April 1966.

(6) We have proposed the structures $N_2Co[P(C_6H_5)_3]_3$ and $H_2Co[P(C_6H_5)_3]_3$ in our previous communications.[1] We consider now the structures shown here with one more hydride to be more reasonable for various reasons which will be published later and wish to revise our previously proposed structures.

(7) Unpublished results.

Lyong Sun Pu, Akio Yamamoto, Sakuji Ikeda
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, Ookayama, Meguro, Tokyo, Japan
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