amidyl-3,5,8-trimethyl-6,7-methylenedioxy-9-hydroxyphenalen-1-one) to photostreptovarone.

Photostreptovarone, $C_{20}H_{17}NO_6$,[3] mp 260–261°, is converted by acidic methanolysis to pyruvic acid, isolated as methyl pyruvate 2,4-dinitrophenylhydrazone, and deptovarone (*dep*yruvylphotostrep*tovarone*, III), $C_{17}H_{15}NO_4$,[3] fine red crystals, dec ~300°, identified as an amine by characteristic infrared absorptions and its ready conversion to a monoacetyl derivative (IV), $C_{19}H_{17}NO_5$,[3] mp 274–275°, and an N,N-dimethyl derivative (V), $C_{19}H_{19}NO_4$,[3] mp 162–163°.

As expected from the molecular formula of II ($C_4H_6O_2$ lost from I), the principal difference between the nmr spectra of I and II (difficultly soluble) is the absence of two methyl singlets near τ 8.0. In the nmr spectrum of the more soluble III, the remaining methyl groups appear as singlets at τ 7.52 (6 H) and 7.81 (3 H). More significant changes from the spectrum of I are the appearance of an aromatic proton at τ 2.33 (singlet) and a sharp methylenedioxy singlet at τ 4.33.[4] In the spectrum of I, these corresponding protons are found at τ 3.45 (olefin singlet) and 4.5 (very broad absorption due to interconversion of conformers, $\Delta G^{\ddagger}_{c} \approx 15.2$ kcal/mole[5]). These changes indicate a side-chain phototransformation. The hydroxyl proton appears at τ −6.51 (streptovarone, τ −4.15).

The infrared spectrum of photostreptovarone (II) retains the pyruvamide (3340, 1725, and 1690 cm^{-1}) and hydrogen-bonded ketone (1625 cm^{-1}) absorptions, but lacks the enol acetate (1767 and 1200 cm^{-1}) and nonhydrogen-bonded carbonyl (1677 cm^{-1}) absorptions of streptovarone (I).

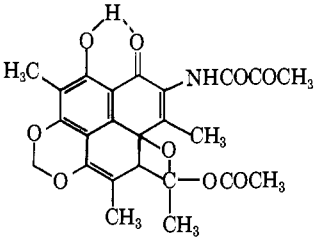
Both nmr and infrared data are in good agreement with structure II. For comparison, the simplest analog, 9-hydroxyphenalen-1-one (VI, synthesized according to Loudon and Razdan[6]), gives a carbonyl band at 1625 cm^{-1} and C-4 proton absorption at τ 2.27 (assigned by factoring the complex AB_2 region of the spectrum of VI[7]). More pertinent is the close similarity of the ultraviolet spectra of II–IV to those of VI and the more complex 9-hydroxyphenalen-1-one derivative atrovenetin triacetate[8] (Table I) and the similar chemical behavior of the chelated hydroxyl group of II–IV and VI: red-brown ferric chloride test,[9] negative boric acid–acetic anhydride test,[10] and lack of reactivity toward acetylation and methylation. The hydroxyl proton of VI is found at τ −6.21.

Table I. Spectra of 9-Hydroxyphenalen-1-ones in Ethanol

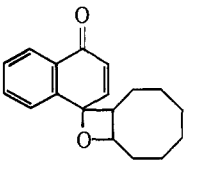
Compound	λ_{max}, mμ (ε)
Photostreptovarone (II)	447 (12,400), 427 (14,400), 407 (12,000), 372 (17,100), 275 (infl), 265 (infl), 237 (31,500)
Deptovarone (III)	460 (4200), 391 (9200), 374 (9200), 288 (4300), 252 (21,000)
Deptovarone (III) (0.1 *N* HCl–ethanol)	448 (4600), 423 (3700), 372 (infl), 360 (7200), 324 (4200), 260 (16,500), 233 (24,000)
Acetyldeptovarone (IV)	445 (10,100), 428 (13,300), 407 (11,700), 373 (17,300), 280 (infl), 265 (infl), 233 (29,100)
9-Hydroxyphenalen-1-one (VI)[a]	440 (12,000), 430 (7400), 415 (8900), 350 (17,800), 265 (8900), 235 (12,600)
Atrovenetin triacetate[a]	433 (19,500), 409 (15,800), 390 (infl), 350–347 (12,000), 275 (17,000), 247 (infl)

[a] Data from ref 8.

The elements lost ($C_4H_6O_3$) upon the irradiation of streptovarone are formally those of acetic anhydride. Such a loss might involve an intermediate such as VII. Although VII has not been isolated, acetic anhydride has been obtained [characterized by glpc retention time (20% S.E. 30 on Chromosorb W column) and infrared and nmr spectra]. Moreover, the intermediate VII resembles the spirooxetans (*e.g.*, VIII) isolated by Bryce-Smith and Gilbert[11] upon irradiation of quinones in the presence of olefins.



VII



VIII

Acknowledgment. This investigation was supported in part by Public Health Service Research Grants No. AI-01278 and AI-04769 from the National Institute of Allergy and Infectious Diseases. We also thank the Upjohn Co. for generous samples of the streptovaricins.

(3) Microanalyses and mass spectra agree with the molecular formulas.

(4) A model is provided by 1,8-methylenedioxynaphthalene, whose spectrum contains a two-proton singlet at τ 4.57.

(5) We thank Dr. J. M. Lehn, Université de Strasbourg, for determination of the temperature-dependent spectra.

(6) J. D. Loudon and R. K. Razdan, *J. Chem. Soc.*, 4299 (1954).

(7) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 16.

(8) D. H. R. Barton, P. deMayo, G. A. Morrison, and H. Raistrick, *Tetrahedron*, **6**, 48 (1959).

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 112.

(10) O. Dimroth and T. Faust, *Chem. Ber.*, 54, 3020 (1921).

(11) D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, 87 (1964).

(12) Public Health Service Predoctoral Fellow and Monsanto Summer Fellow.

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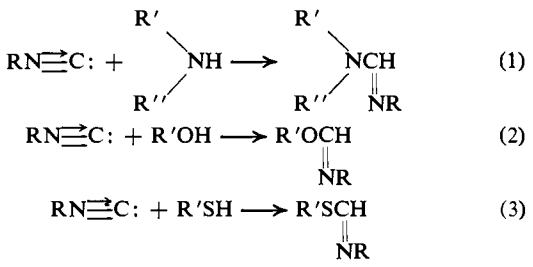
Synthetic Reactions by a Complex Catalyst. VI. A Novel Hydrosilation of Isocyanide by Copper Catalyst

Sir:

In the course of studies upon synthetic reactions of compounds of carbon having lone-pair electrons,[1] we have recently found that, in the presence of copper catalyst, isocyanide reacts with primary and secondary amines,[1a] alcohols,[1d] and thiols[2] to produce the corresponding derivatives of formimidic acid. These reactions involve insertion of isocyanide into nitrogen–hydrogen, oxygen–hydrogen, and sulfur–hydrogen linkages, respectively; on the other hand, these are con-

(1) (a) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Letters*, 6121 (1966); (b) T. Saegusa, S. Kobayashi, K. Hirota, and Y. Ito, *ibid.*, 6125 (1966); (c) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and T. Shimizu, *ibid.*, 6131 (1966); (d) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *ibid.*, 521 (1967).

(2) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and Y. Okumura, to be published.



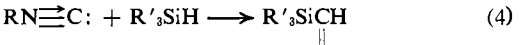
(1)

(2)

(3)

sidered to be α,α additions of amine, alcohol, and thiol to the carbon atom of isocyanide.

The present communication describes the reaction of isocyanide with trialkylsilane by a copper compound catalyst in which the isocyanide carbon atom is inserted between silicon and hydrogen of the silane compound.



(4)

The product of formimidoylsilane is the adduct of $\equiv$SiH to isocyanide, and the reaction may be regarded as a novel hydrosilation, which is interestingly compared to the hydrosilation of olefins with group VIII metal complex catalysts.[3,4]

Under nitrogen atmosphere, a mixture of 12 ml (100 mmoles) of cyclohexyl isocyanide, 13.5 ml (120 mmoles) of trimethylsilane, 0.52 g (2 mmoles) of copper(II) acetylacetonate, and 10 ml of benzene (reaction solvent) was heated at 100° for 5 hr in a sealed tube. As the temperature was raised, the catalyst was gradually dissolved in the reaction mixture to form a homogeneous system at 100°. After the reaction, the mixture was distilled to isolate N-cyclohexylformimidoyltrimethylsilane (I), bp 118–120° (40 mm). *Anal.* Calcd for $C_{10}H_{21}NSi$: C, 65.50; H, 11.54; N, 7.64. Found: C, 65.19; H, 11.89; N, 7.62. The yield of I based on cyclohexyl isocyanide was 86%. The new silicon compound (I) is a colorless liquid and stable under dry nitrogen atmosphere, but vulnerable to moisture.

(3) (a) J. L. Speier, L. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957); (b) J. L. Speier and J. C. Saam., *ibid.*, **80**, 4104 (1958); (c) *ibid.*, **83**, 1351 (1961); (d) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964).

(4) A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 16 (1965).

$(CH_3)_3SiCH{=}N\text{-}c\text{-}C_6H_{11}$

I

The structure of I was convincingly confirmed by infrared, ultraviolet, and nmr spectra as well as by the reduction product. The infrared spectrum of I (neat) was consistent with the assigned structure, showing $-Si(CH_3)_3$ at 1246 and 842 cm^{-1} and $>C{=}N-$ at 1601 cm^{-1}. The ultraviolet spectrum of I in cyclohexane had an absorption of λ_{max} 285 mμ (ϵ 70), which is assigned to the $n \rightarrow \pi^*$ transition of the $>C{=}N-$ group. The nmr spectrum in $CDCl_3$ showed a singlet at τ 1.67 (1 H, $-CH{=}N-$), two broad signals centered at τ 7.2 (1 H, $=NCH<$) and 8.5 (10 H, $-(CH_2)_5-$ of the cyclohexane ring), and a singlet at τ 9.87 (9 H, $-Si(CH_3)_3$). Further evidence supporting structure I was obtained in the treatment of I with lithium aluminum hydride in ether at room temperature, which afforded N-(trimethylsilylmethyl)cyclohexylamine (II), bp 208–210° (lit.[5] bp 211°), $n^{25}D$ 1.4520 (lit.[5] $n^{25}D$ 1.4519). The structure

$$\text{I} \xrightarrow[\text{in ether}]{\text{LiAlH}_4} (CH_3)_3SiCH_2NH\text{-}c\text{-}C_6H_{11}$$

II

of II was further confirmed by infrared and nmr spectra. Similar results were obtained with cupric chloride as catalyst.

The catalytic activity of copper compounds in reaction 4 seems quite specific. In the absence of copper catalyst both trimethylsilane and isocyanide were recovered unchanged from the heat-treated reaction mixture. Further, no reaction was observed in the presence of chloroplatinic acid, which is known to be an efficient catalyst of hydrosilation of olefins,[3] as catalyst.

Reactions of various silane compounds with isocyanide by copper catalyst and mechanistic studies are now being carried out.

(5) J. E. Noll, J. L. Speier, and B. F. Daubert, *ibid.*, **73**, 3867 (1951).

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Additions and Corrections

The Crystal Structure of Azulene-1,3-dipropionic Acid [*J. Am. Chem. Soc.*, **88**, 4794 (1966)]. By HERMAN L. AMMON and M. SUNDARALINGAM. Department of Biological Structure, University of Washington, Seattle, Washington.

The fifth sentence of the first paragraph (beginning on line 13 of column 1, page 4794) should be changed to read as follows: The precision of the structure analysis was not seriously affected because an allowance was made for the disorder during the refinement; it was estimated[7] that failure to consider the alternate orientation would have produced bond length differences no greater than 0.014 A from those reported for the corrected structure.

In Table V, the length of the C(4)–C(10) bond in the azulene–*sym*-trinitrobenzene complex is not 1.382 as reported, but 1.392. This change affects footnote *a* to Table V. In the second sentence ("T = 12.68 . . ."), the value 12.68 should be replaced with 14.64 and 0.32 should be replaced with 0.21.

The Determination of the Concentration of Hydrolytic Enzyme Solutions: α-Chymotrypsin, Trypsin, Papain, Elastase, Subtilisin, and Acetylcholinesterase [*J. Am. Chem. Soc.*, **88**, 5890 (1966)]. By MYRON L. BENDER, MARIA LUISA BEGUÉ-CANTÓN, ROBERT L. BLAKELEY, LEWIS J. BRUBACHER, JOSEPH FEDER, CLAUDE R. GUNTER, FERENC J. KÉZDY, JOHN V. KILLHEFFER, JR., THOMAS H. MARSHALL, CHARLES G. MILLER, ROGER W. ROESKE, and JAMES K. STOOPS. Division of Biochemistry of the Department of Chemistry, Northwestern University, Evanston Illinois, and the Department of Biochemistry, Indiana University, School of Medicine, Indianapolis, Indiana.