Acknowledgment. We thank Johnson-Matthey Co. (United Kingdom) for a loan of platinum(II) chloride.

M. A. Bennett,* G. B. Robertson, P. O. Whimp, T. Yoshida
Research School of Chemistry
The Australian National University
Canberra, A.C.T. 2600, Australia

Received January 22, 1973

Homogeneously Catalyzed Hydration of Nitriles to Carboxamides

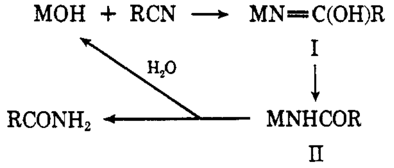
Sir:

Metal ions such as Ni^{2+} or Cu^{2+} catalyze the hydration of the C≡N function in 2-cyanopyridine[1,2] and 2-cyano-1,10-phenanthroline[3] to give the corresponding carboxamides, and the pentaamminecobalt(III) complexes of benzonitrile, and 3- and 4-cyanophenol are hydrated in alkaline solution to the corresponding *N*-carboxamido complexes.[4] Coordination through the pyridine function in the first two cases and through the nitrile function in the last case is thought to assist nucleophilic attack by hydroxide ion, although coordinated OH is also known to be effective for the hydration of aminoacetonitrile to glycine in Co(III) complexes.[5] We present a preliminary report on the hydration of simple aliphatic nitriles to the corresponding carboxamides under neutral conditions homogeneously catalyzed by planar, nonionic tertiary phosphine metal–hydroxy complexes.

A mixture of $Pt(C_6H_8)(diphos)$ (**1**)[6,7] (0.067 g, 0.1 mmol), acetonitrile (5 ml), and water (2 ml) heated under reflux for 3 hr gives 0.105 g of acetamide (17 mol per mol of catalyst). The catalyst is converted into a *N*-acetamido–platinum(II) complex which has not yet been conclusively identified. Under similar conditions, $Pt(C_6H_8)[P(C_6H_5)_3]_2$[7] gives 58 mol of acetamide per mol of catalyst after 16 hr, together with the *N*-acetamido complex $Pt(C_6H_9)(NHCOCH_3)[P(C_6H_5)_3]_2$ (**3**) (40% yield based on Pt). Other catalysts for the hydration of acetonitrile include **3** (35 mol per mol, 5 hr), *trans*-$Pt(CH_3)(NHCOCH_3)[P(C_6H_5)_3]_2$ (**4**) (75 mol/mol, 2.5 hr), $Pt(C_6H_9)(OH)(diphos)$[8] (**5**) (6.8 mol/mol, 1 hr), and *trans*-$Ir(OH)(CO)[P(C_6H_5)_3]_2$[9-11] (**6**) (25 mol/mol, 20 hr). The most efficient catalyst for the hydration of acetonitrile and propionitrile is *trans*-$Rh(OH)(CO)[P(C_6H_5)_3]_2$ (**7**)[9,10] which gives 150 mol of acetamide and 200 mol of propionamide per mol of catalyst after refluxing for 3 hr. **7** also catalyzes the hydration of phenylacetonitrile, acrylonitrile, and crotonitrile to the corresponding carboxamides, but is ineffective for benzonitrile. In contrast, heating **1** under reflux with benzonitrile, water, and toluene for 15 hr gives a mixture of benzamide (0.9 mol per mol) and the *N*-benzamido complex $Pt(C_6H_9)(NHCOC_6H_5)(diphos)$ (**8**) (43% yield based on Pt). In no case has further hydrolysis of the amide to the carboxylic acid been observed.

The catalytic ability of the cyclohexyne complexes **1** and **2** depends on their reaction with water to give hydroxy complexes; *e.g.*, **5** can be isolated by reaction of water with **1**.[8] The fact that *N*-amido complexes can be isolated from some of the catalytic reactions and that these complexes also function as hydration catalysts implicates them in the catalytic cycle. We suggest that the reaction involves insertion of the nitrile into the M–OH bond (Scheme I) to give an N-bonded imino–alcohol complex (I),[12] which rapidly rearranges to the *N*-amido complex (II). Addition of water to (II) regenerates the M–OH bond, thus completing the catalytic cycle. It is not known whether the insertion step involves a five-coordinate intermediate or whether hydroxide is first displaced from the coordination sphere to give an ionic complex. However, the M–OH bond is essential for the process, because *trans*-$[Pt(CH_3)(CH_3CN)\{P(C_6H_5)_3\}_2]BF_4$ does not catalyze the formation of acetamide from acetonitrile and water.

Scheme I. Catalytic Hydration of Nitriles[a]



[a] Other ligands on the metal atom M are omitted for clarity.

The platinum complex **1** differs from complexes **4**, **6**, and **7** in its ability to catalyze hydration of the olefinic double bonds of α,β-unsaturated nitriles in addition to that of the C≡N bonds. Thus, a mixture of **1** (0.067 g, 0.1 mmol), acrylonitrile (4 ml), and water (2 ml) heated at 100° for 16 hr gives 1.05 g of a mixture containing 85% β,β′-dicyanoethyl ether, 8% acrylamide, and 7% ethylene cyanohydrin, the main product presumably being derived by cyanoethylation of ethylene cyanohydrin. Under similar conditions, crotonitrile is converted into a mixture of $CH_3CH(OH)CH_2CN$ and $CH_3CH{=}CHCONH_2$, plus other as yet unidentified products.

We are currently examining the scope of these reactions using a range of nitriles and other unsaturated organic compounds. Catalysts of the type described here could prove to be a useful supplement to the usual catalysts employed for nitrile hydration, *i.e.*, acid, base, or weakly basic hydrogen peroxide,[13] if groups sensitive to these reagents are also present in the nitrile.

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(1) P. F. B. Barnard, *J. Chem. Soc. A*, 2140 (1969).

(2) S. Komiya, S. Suzuki, and K. Watanabe, *Bull. Chem. Soc. Jap.*, **44**, 1440 (1971).

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(5) D. A. Buckingham, A. M. Sargeson, and A. Zanella, *ibid.*, **94**, 8246 (1972).

(6) C_6H_8 = cyclohexyne; C_6H_9 = σ-cyclohexenyl; diphos = 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

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(8) M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *ibid.*, **95**, 3028 (1973).

(9) G. Gregorio, G. Pregaglia, and R. Ugo, *Inorg. Chim. Acta*, **3**, 89 (1969).

(10) L. Vaska and J. Peone, Jr., *Chem. Commun.*, 418 (1971).

(11) G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *ibid.*, 758 (1971).

(12) Compare the nucleophilic attack of methanol on coordinated pentafluorobenzonitrile in *trans*-$[Pt(CH_3)(C_6F_5CN)\{P(CH_3)_2(C_6H_5)\}_2]^+$ to give an imino–ether complex *trans*-$[Pt(CH_3)\{NH{=}C(OCH_3)(C_6F_5)\}\{P(CH_3)_2(C_6H_5)\}_2]$: H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971). These authors consider that side-on bonding of C_6F_5CN is a prerequisite for nucleophilic attack, but this seems unlikely for the aliphatic and aromatic nitriles we have studied.

(13) F. C. Schaefer in "The Chemistry of the Cyano Group," Z. Rappoport, Ed., Interscience, New York, N. Y., 1970, pp 256–263.

Acknowledgment. We thank Johnson-Matthey (United Kingdom) for a loan of platinum metal salts.

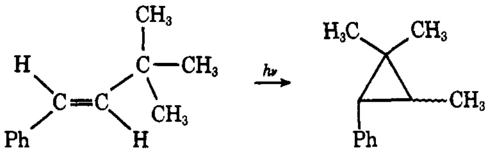
M. A. Bennett,* T. Yoshida
Research School of Chemistry, Australian National University
Canberra, ACT 2600, Australia

Received January 22, 1973

Photochemical Rearrangement of β-*tert*-Butylstyrenes. Stereochemistry

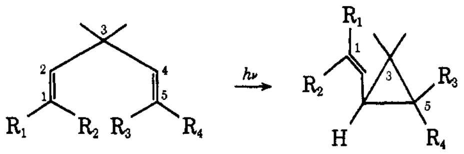
Sir:

The photochemical rearrangement of β-*tert*-butylstyrene (**1**) to trimethylphenylcyclopropane (**2**), a reaction discovered by Griffin[1] some years ago, is an intriguing one for several reasons. From one point of view the process may be looked upon as a 1,2 migration of a methyl group to the (presumably) radical-like β carbon of the excited state styryl group, a transformation which has little analogy in ground-state chemistry where migration of saturated carbon occurs only to cationic centers.[2] From another aspect, the reaction is formally analogous to the di-π-methane rearrangement,[3] in which unsaturated carbon undergoes a similar photochemical 1,2 shift. Both are formally ${}_{\sigma}2 + {}_{\pi}2$ cycloadditions and may proceed in a concerted fashion in the excited state with either ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ or ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$ stereochemistry.[4]



1 **2** (1)

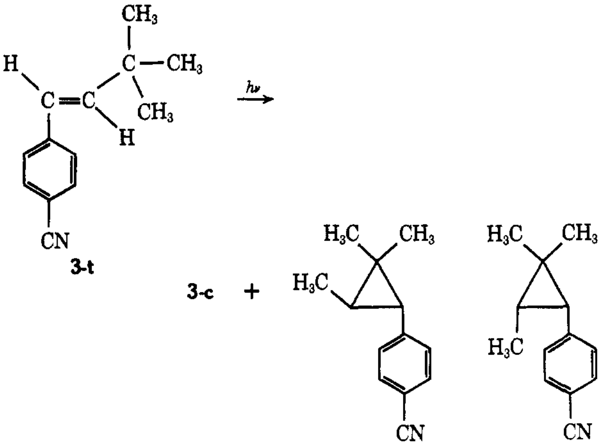
The stereochemistry of the divinylmethane rearrangement, a particular case of the di-π-methane, has been investigated in some detail.[3,5,6] Of the three centers of stereochemistry involved, the reaction has been found to proceed with inversion at C-3[5,6] and retention at C-1[3] and C-5,[6] consistent with a concerted ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ excited state process (eq 2).



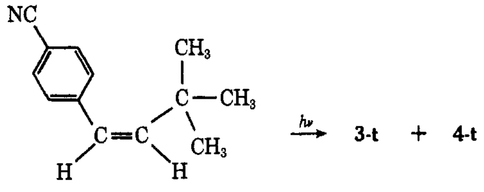
(2)

However, it seems likely that the divinylmethane rearrangement is not a simple ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ reaction, but rather use is made of both systems in a ${}_{\sigma}2_{a} + {}_{\pi}2_{a} + {}_{\pi}2_{a}$ process.[7] This cannot be true for **1**. Thus, an investigation of the stereochemistry of process 1 was inviting. We present here an analysis of the stereochemistry at C-1.

Experimental difficulties (*vide infra*) precluded an accurate assessment of the stereochemistry of the reaction of **1** itself. However, it was feasible to do so with the para cyano derivative **3**.[8] Under preparative irradiation conditions **3-t** produces rapidly a mixture of **3-c** and **3-t** and, more slowly, a mixture of cyclopropanes **4-t** and **4-c**. The cyclopropanes do not accumulate to any great extent due to their very efficient further transformation to olefins.[1,9] Nonetheless, it was possible to isolate the mixture of **4-t** and **4-c** by preparative gc and show they were identical (nmr and ir spectra; gc retention times) with a mixture prepared independently.[8,10]



3-t **4-t** **4-c**



3-c

Quantitative irradiations[8] starting with pure **3-c** and **3-t** were carried to very low conversions: 1–2% to the other isomer; <0.2% to cyclopropane. Remarkably, at these low conversions, both **3-c** ($\Phi = 0.0070$) and **3-t** ($\Phi = 0.0026$) gave **4-t** as the only observable cyclopropane. We could detect no **4-c** in either case; our separation and detection limits are such that we can say cyclopropane **4** is formed with at least 93% trans stereochemistry.

Both reactions are singlet state processes since xanthone sensitization results only in trans–cis isomeriza-

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[1] H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966).

[2] (a) H. E. Zimmerman in "Molecular Rearrangements, Part One," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 394–399, and references therein. (b) Recently an example of an apparent radical rearrangement involving a 1,2-alkyl shift has been observed; see C. Walling and A. Cioffar, *J. Amer. Chem. Soc.*, **94**, 6064 (1972). As Walling notes, 1,2-alkyl rearrangements in biradicals are well-substantiated phenomena.

[3] H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972), and references therein.

[4] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 98–99.

[5] P. S. Mariano and J. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1971).

[6] H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969).

[7] (a) H. E. Zimmerman and R. D. Little, *ibid.*, **94**, 8256 (1971); (b) H. E. Zimmerman, P. Hackett, D. F. Jeurs, J. M. McCall, and B. Schroder, *ibid.*, **93**, 3653 (1971).

[8] Synthetic and experimental details will be presented in a full paper.

[9] (a) H. Kristinsson and G. W. Griffin, *Tetrahedron Lett.*, 3259 (1966); (b) P. H. Mazzochi, R. S. Lustig, and G. W. Craig, *J. Amer. Chem. Soc.*, **92**, 2168 (1970).

[10] Cyclopropane configurations were readily assigned by the method of Closs and Moss.[11] The signals due to the methyl groups in 3-c and 3-t are very similar to those in the unsubstituted cyclopropanes (2).

[11] G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).