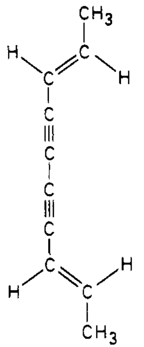
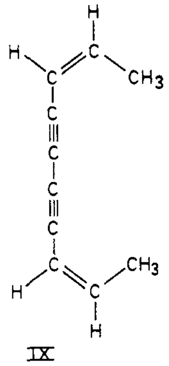
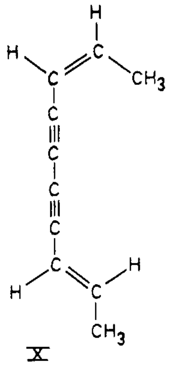
cyclohexa-1,3-diene takes place at 130°;[9,10] the *trans,cis,-cis* and *all-cis* isomers are still less reactive.

Oxidative coupling with $Cu(OAc)_2$–pyridine converted *cis-* and *trans*-3-penten-1-ynes, and a mixture of these two, into the three stereoisomers VIII–X of 2,8-decadiene-4,6-diyne which were purified by preparative glpc (Apiezon L, 6-m column, 136°).[11]


VIII


IX


X

The hydrogenation of the pure (glpc) decadienediynes in pentane at −20° in the presence of Lindlar catalyst was stopped after uptake of 2.4 moles of hydrogen. Although glpc showed mixtures of at least 14 components,[12] at −70° the three decatetraenes I, II, and V crystallized in a pure state. The three tetraenes polymerized so rapidly in the presence of oxygen that all operations had to be carried out under nitrogen.

Some physical properties are: I: mp 30–32°; ir ($CCl_4$): *cis*-CH═CH 650 $cm^{-1}$, *trans*-CH═CH 947 $cm^{-1}$; uv (pentane): 307.5 mμ (log ε 4.48),[13] 294 (4.57), 281.5 (4.40), 272 and 261 shoulders (4.15, 3.89); nmr ($CDCl_3$):[14] $\tau$ 8.20 (d, $J$ = 6.6 cps, further split by long-range coupling) for two methyls, 3.0–4.7 (m) for eight vinyl hydrogens; II:[15] mp 61–63°; ir ($CCl_4$): *cis*-CH═CH 685 $cm^{-1}$; uv (cyclohexane): 317 mμ (log ε 4.48), 302.5 (4.58), 289.5 (4.44), 280 and 269 shoulders (4.24, 4.02); nmr ($CDCl_3$): $\tau$ 8.23 (d, $J$ = 6.9 cps, further split by long-range coupling) for two methyls, 4.46 ($\propto$) for 2- and 9-H, ≈3.7 (s, broad) for six vinyl hydrogens; V: mp below 0°; ir ($CCl_4$): *cis*-CH═CH 698 $cm^{-1}$, *trans*-CH═CH 950 $cm^{-1}$; uv (cyclohexane): 313 mμ (log ε 4.28), 299 (4.40), 286.5 (4.29), 277 and 264 shoulders (4.09, 3.99); nmr ($CDCl_3$): $\tau$ 8.18 (d, $J$ = 6.0 cps, broad signals) for two methyls, 2.9–4.7 (m) for eight vinyl hydrogens.

Cyclization of I gave III:[5] nmr ($CDCl_3$): $\tau$ 9.0 (three signals, partial coalescence) for two methyls, ≈7.6 (m) for 7- and 8-H, 3.39–4.38 (m) for six vinyl hydrogens. Ozonolysis in ethyl acetate at −60°, peracetic acid treatment, and reaction of acidic products with diazomethane yielded dimethyl *rac*-2,3-dimethylsuccinate, bp 95° (12 mm), identical with an authentic specimen (ir, glpc retention time).

The isomerization III → IV[16] in $CHCl_3$ at 20° went to completion; IV: bp 49° (10 mm); ir ($CCl_4$): *cis*-CH═CH 710 $cm^{-1}$; uv (cyclohexane): 274 mμ (log ε 3.40), spectrum similar to that of the unsubstituted compound;[17] nmr ($CDCl_3$): $\tau$ 8.93 (d, $J$ = 6.3 cps) and 8.98 (d, $J$ = 5.9 cps) for two methyls. IV combines with TCNE at 0° in ethyl acetate to give a Diels–Alder adduct,[11,18] mp 205–206°; nmr ($CDCl_3$): $\tau$ 9.03 (d, $J$ = 8.0 cps) and 8.97 (d, $J$ = 8.0 cps) for two methyls, 8.20 (q, 1 H), 7.67 (q, 1H).

The conversion II → IV was completed in $CDCl_3$ at 65° after 14 hr.[5] Kinetic measurements were conducted in sealed nmr tubes by following the disappearance of the methyl doublet of II (II + IV = 100%): $10^4k$ ($sec^{-1}$) at 72.1°: benzene 3.70, $CCl_4$ 3.45, $CDCl_3$ 2.92.

From the mixture of 90% VI and 10% VII, which was obtained from V at 9° in $CDCl_3$ after 155 hr, the bicyclic tautomer VII was removed at −10° by reaction with azodicarboxylic acid N-phenylimide as a crystalline Diels–Alder adduct; nmr of pure VI ($CDCl_3$): $\tau$ 8.95 (d, $J$ = 6.9 cps) for two methyls, 7.25 (m) for 7- and 8-H, ≈4.15 (s, broad) for six vinyl hydrogens.

The equilibrium mixture of VII and VI showed bp 50–53° (11 mm) and *cis*-CH═CH wagging at 690 $cm^{-1}$; nmr ($CDCl_3$) of *cis*-7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (VII): $\tau$ 8.97 (d, $J$ = 6.4 cps) for two methyls, 7.44 (s, broad) for 7- and 8-H, 7.25 (m) for 1- and 6-H, 4.28 (s, broad) for four vinyl hydrogens; TCNE adduct of VII,[11,18] mp 223–224°; nmr (acetone-$d_6$): $\tau$ 8.92 (d, $J$ = 6.6 cps) for two methyls, 7.90 (m, 2 H).

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[9] E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Letters*, 385 (1965).

[10] E. Vogel, W. Grimme, and E. Dinné, *ibid.*, 391 (1965).

[11] Nmr and infrared spectra are in accordance with the structures. A full account of these data will be published later.

[12] The hydrogenation products contained 52% I, 52% II, and 38% V, respectively.

[13] Extinction coefficients are not reliable because of fast rearrangement to III with its weaker absorption.

[14] Determined on a Varian A-60 with TMS as internal standard, I, II, III, and V at −40°; s denotes singlet, d doublet, q quadruplet, $\propto$ octuplet, m multiplet.

[15] D. Holme, E. R. H. Jones, and M. G. Whiting, *Chem. Ind.* (London), 928 (1956).

[16] D. A. Bak and K. Conrow, *J. Org. Chem.*, **31**, 3958 (1966), described mixtures enriched in IV + VII.

[17] A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

[18] Satisfactory elementary analyses have been obtained.

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*Received October 27, 1967*

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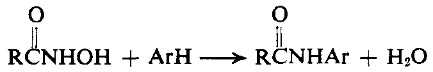
## Direct Amidation. A New Aromatic Substitution Process

*Sir:*

A traditional method for the preparation of acyl derivatives of aromatic amines employs sequential nitration, reduction, and acylation of an aromatic starting material. We report here a new and promising method for the direct introduction of an acylamido group onto a moderately reactive aromatic ring in a single step.

We have found that an aromatic compound and a hydroxamic acid interact in hot polyphosphoric acid to furnish directly an acylamido derivative of the aromatic compound. In the simplest cases, the products are



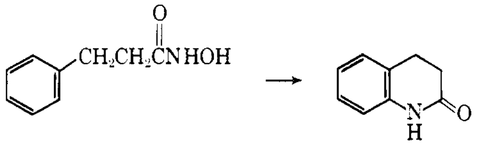
$$R\overset{O}{\overset{\|}{C}}NHOH + ArH \longrightarrow R\overset{O}{\overset{\|}{C}}NHAr + H_2O$$

easily obtained from the diluted reaction mixture by extraction. Moreover, the operation is simple and can be completed in a short time.

One of the more successful examples that we have uncovered involves an intramolecular ring closure. Specifically, when hydrocinnamohydroxamic acid[1] was

[1] C. D. Hurd and L. Bauer, *J. Am. Chem. Soc.*, **76**, 2791 (1954).

heated in polyphosphoric acid (165–170°, 40 min), hydrocarbostyril was produced in 79% yield.



Intermolecular amidations can be successfully carried out if a large excess of the hydroxamic acid is employed. For example, anisole can be converted to *p*-acetanisidide in 57% yield by the gradual addition of 10 equiv of acetohydroxamic acid[2] to a hot mixture of anisole in polyphosphoric acid. Sharply reduced yields resulted when equimolar amounts of acetohydroxamic acid and anisole were used. Significantly, the crude products from the direct amidation of such monosubstituted benzene derivatives as toluene and anisole were nearly free of *ortho-* and *meta-*substituted isomers.

The mechanism of the direct amidation transformation is uncertain. One possibility which presently appears attractive is a rationalization in terms of an intermediate ketoxime or its conjugate acid. An aromatic compound and a carboxylic acid react in polyphosphoric acid to furnish a ketone;[3,4] in a parallel fashion, an aromatic compound and a hydroxamic acid may be expected to react in the same medium to furnish a ketoxime. A ketoxime, however, can have only a fleeting existence, for it is rapidly and efficiently transformed in the hot acid medium to an amide by a Beckmann rearrangement.[3,4]

$$R\overset{O}{\overset{\|}{C}}NHOH \longrightarrow R\overset{HON}{\overset{\|}{C}}Ar \longrightarrow R\overset{O}{\overset{\|}{C}}NHAr$$

It is apparent that direct amidation is a promising synthetic method. We are continuing our investigations of the scope and versatility of the reaction.

**Acknowledgment.** Support of this research by a grant from the University of Connecticut Research Foundation is gratefully acknowledged.

(2) A. Hantzsch, *Ber.*, **27**, 799 (1894).
(3) F. Uhlig and H. R. Snyder, *Advan. Org. Chem.*, **1**, 35 (1960).
(4) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958).
(5) University of Connecticut Predoctoral Fellow, 1966–1967.

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## Phenylrhodium Tetraphenylporphine. A Novel Synthesis of a Rhodium–Carbon $\sigma$ Bond

*Sir:*

Compounds containing alkyl- and aryl–metal bonds are usually synthesized by use of Grignard reagents or aryllithium compounds, or by a reaction of a low oxidation state of the metal with alkyl halides.[1–8] We report the synthesis and characterization of a compound containing a rhodium–phenyl $\sigma$ bond.

Tetraphenylporphine (TPP) and $[Rh(CO)_2Cl]_2$ are refluxed for 10 hr in benzene, and the compounds in the resulting solution are separated by chromatography on an alumina column. The RhTPP fraction[9] gives purple crystals on standing. This new compound contains a $\sigma$-bonded phenyl group and can best be represented as $C_6H_5Rh^{IV}TPPCl$.[10] The compound is paramagnetic with a room-temperature susceptibility, $\mu_{eff} = 1.95$ BM.

The characterization of this new metalloporphyrin was accomplished by a three-dimensional X-ray structure determination. The crystal is monoclinic with cell constants $a = 17.33$, $b = 13.09$, $c = 23.28$ Å, $\gamma = 124.8°$. The space group of the crystal is $P2_1/a$ with four molecules per unit cell. The X-ray data were obtained by use of the automatic diffractometer PAILRED with Mo K$\alpha$ radiation. There were 2382 observed intensities[11] used in the structure analysis. The structure was solved by the symbolic addition method[12–14] employing the computer program MAGIC.[15]

The structure was refined by Fourier and least-squares techniques. The final $R$ factor[16] including all reflections with isotopic temperature factors for the 56 atoms (hydrogen atoms not included) is 10.9%. The tetraphenylporphine part of the molecule is similar to other porphyrin structures that have been recently determined.[17–20]

The porphyrin has the usual local planarity of the pyrrole rings and the phenyl rings, but the over-all porphyrin skeleton is nonplanar with respect to the best plane defined by the four pyrrole nitrogen atoms. It is of particular interest that the rhodium atom lies in the plane of the four nitrogen atoms. This observation may help in the interpretation of the iron position in hemoglobin and myoglobin, as these compounds undergo the transformation from the deoxy high-spin to the oxygenated low-spin complexes.[21,22]

(1) R. Bonnett, *Chem. Rev.*, **63**, 573 (1963).
(2) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).
(3) J. Halpern and J. Maher, *ibid.*, **86**, 2311 (1964).
(4) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 772 (1961).
(5) J. Chatt and B. L. Shaw, *ibid.*, 285 (1961).
(6) A. Cope and R. Gourley, *J. Organometal. Chem.* (Amsterdam), **8**, 527 (1967).
(7) D. A. Clarke, R. Grigg, and A. W. Johnson, *Chem. Commun.*, 208 (1967).
(8) D. A. Clarke, R. Grigg, A. W. Johnson, and H. A. Pinnock, *ibid.*, 309 (1967).
(9) E. Fleischer and N. Sadasivan, *ibid.*, 159 (1967).
(10) *Anal.* Calcd for $C_{50}H_{33}N_4RhCl\cdot H_2O$: C, 71.0; H, 4.3; N, 6.6; Rh, 12.2. Found: C, 71.9; H, 4.7; N, 5.9; Rh, 12.8. The representation of the rhodium as a +4 oxidation state is only a formalism. The details of the electronic structure of this compound are being studied.
(11) The yield of 25% of the intensities within the copper sphere is due to several reasons. The diffraction of the small crystal used in obtaining the data made it inadvantageous to collect outside a sphere with $2\theta > 50°$. A region containing 3700 peaks was investigated yielding the 2382 "observed" intensities, or a 65% yield. The structure showed no evidence of large thermal motion (isotropic temperature factors $B$ were in the range of 2–4 Å$^2$) nor of general disorder (there is a $H_2O$ solvent that either is disordered or has a large thermal motion).
(12) D. Sayre, *Acta Cryst.*, **5**, 60 (1952).
(13) W. H. Zachariasen, *ibid.*, **5**, 68 (1952).
(14) J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966).
(15) See A. Stone Ph.D. Thesis, University of Chicago, 1967, for a description of the program MAGIC written by a A. Stone and R. Dewar.
(16) $R = \Sigma||F|_o - |F|_c|\Sigma|F|_o$; the average standard deviation in the C–C bond distances is 0.03 Å. The average C–C bond distance for all phenyls is 1.39 Å.
(17) E. B. Fleischer, L. Webb, and C. Miller, *J. Am. Chem. Soc.*, **86**, 2342 (1964).
(18) E. B. Fleischer and L. Webb, *J. Chem. Phys.*, **43**, 3100 (1965).
(19) E. B. Fleischer and A. Stone, *Chem. Commun.*, 332 (1965).
(20) S. J. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **89**, 3331 (1967).
(21) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *ibid.*, **87**, 2312 (1965).
(22) J. L. Hoard in "Hemes and Hemoproteins," B. Chance, R. Esterbrook, and T. Yonetani, Ed., Academic Press Inc., New York, N. Y., 1966, p 9.