2,7 was isolated in ~3% yield [bp 85° (1 mm)]. Phenoxyoctadiene absorbs 1.96 moles of hydrogen to give *n*-octyl phenyl ether, which was independently synthesized from sodium phenoxide and *n*-octyl bromide. The double bond positioning at 2 and 7 was clearly indicated from the nmr spectrum [δ 1.5 ppm (2 H), $-CH_2-$; 2.0 (4 H), $=CCH_2-$; 4.3 (2 H), $-OCH_2C=$; 4.9 (2 H), $=CH_2$; 5.6 (3 H), $=CH-$; δ ~7.0 (5 H), C_6H_5] from which it was evident that one double bond was terminal and the other allylic to the phenoxy group, but with no methyl groups branched or terminal in the product. The infrared spectrum supports these conclusions (10.1 and 10.95 μ, $-CH=CH_2$; 10.35 μ, *trans*-$CH=CH-$).

Though $(pyr)_2PdCl_2$ was isolated from the reaction mixture and proved to be an active catalyst, no variation of neutral or anionic ligand was superior or raised the conversion of phenol to compound I above 30%. The addition of a stronger base made a profound difference. When phenol (0.4 mole) and butadiene (1.7 moles) were heated at 100° in the presence of palladium chloride (concentrations as low as 5.6×10^{-4} *M*) and sodium phenoxide (1.4×10^{-2} *M*), a 96% conversion of phenol to 1-phenoxyoctadiene-2,7 (I, XR = OC_6H_5, selectivity ~91% *trans*, ~4% *cis*) and 3-phenoxyoctadiene-1,7 (II, XR = OC_6H_5, ~5%) resulted. Phenoxyoctadiene was not obtained from butadiene, phenol, and sodium phenoxide.

There are several remarkable things about this reaction. It is simple, fast, free of significant by-products, and indifferent to the usual poisons. It can be run at elevated temperatures (100 or 150°) under pressure or at reduced temperature (~0°) at atmospheric pressure without change of product, product distribution, or phenol conversion. The reaction can be run with equal success in the presence or absence of solvent (in acetonitrile or chloroform, etc., 100% yield of phenoxyoctadiene). A wide variety of palladium catalysts (*e.g.*, π-allylpalladium chloride or bis(benzonitrile)palladium chloride with sodum phenoxide, etc.) have also been used and proved to be efficient, participating in long catalytic chains. Other metal complexes of group VIII are also effective (*e.g.*, Ru, Pt). The reaction is generally most successful with excess butadiene (phenol:butadiene, 1:4). Other phenols react with butadiene with equal ease (yields 50–100%), giving substituted phenoxyoctadienes (*p*-Cl, *p*-CH_3, *p*-OMe, 2,6-dimethyl, 2,4-dichloro, etc.). Isoprene also participates in the reaction and gives a mixture of phenoxydecadienes.

Related homogeneously catalyzed oligomerizations of butadiene with alcohols, amines, and carboxylic acids have all been realized in excellent yield.[6] The products contain the terminally substituted 8-carbon chain as the predominant isomer.

Butadiene dimerizations in the presence of transition metals to cyclic or branched products are only a recent development.[7] The linear dimerization of butadiene in the presence of a palladium catalyst and a nucleophile also serves as a convenient and easy source of an inaccessible butadiene dimer. Under suitable conditions, phenoxyoctadiene can be converted to 1,3,7-octadiene (III) in good yields and conversions.[5,8] Thus when phenoxyoctadiene was formed at about 0° from phenol (0.106 mole), butadiene (0.42 mole), π-allylpalladium chloride (0.001 mole), and sodium phenoxide (0.0028 mole), and triphenylphosphine (0.0042 mole) was added to the reaction mixture before distillation at reduced pressure, 1,3,7-octatriene (98% pure) was obtained in 85% yield.

Octatriene (bp 122°) is a colorless liquid that slowly polymerized when left in the air unstabilized. The infrared and nmr data [δ ~2.2 ppm (4 H), $=CCH_2-$; 4.8–5.3 (4 H), $CH_2=$; 5.4–6.9 (4 H), $=CH-$] confirm the absence of terminal methyl groups and the ultraviolet spectrum [λ_{max} 226 mμ (ϵ 22,700)] and mass spectroscopic fragmentation pattern are consistent with a linear structure with two double bonds conjugated.[9]

The possible mechanism and further extensions of this reaction will be published shortly.[10]

Acknowledgment. The author expresses his thanks to D. W. Wood for experimental assistance.

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(7) G. Wilke, Belgium Patent 598,363 (1960); S. Otsuka, T. Kikuchi, and T. Taketomi, *J. Am. Chem. Soc.*, **85**, 3709 (1963); T. Saito, Y. Uchida, and A. Misono, *Bull. Chem. Soc., Japan*, 37, 105 (1964); D. Wittenberg, *Angew. Chem. Intern. Ed. Engl.*, 3, 153 (1964); T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, 87, 5638 (1965); H. Takahashi, S. Tai, and M. Yamaguchi, *J. Org. Chem.*, 30, 1661 (1965); H. Muller, D. Wittenberg, H. Seigt, and E. Scharf, *Angew. Chem. Intern. Ed. Engl.*, **4**, 327 (1965); H. Seibt and N. von Kutepow, U. S. Patent 3,277,099 (Oct 4, 1966).

(8) E. J. Smutny and H. Chung, unpublished results.

(9) G. B. Butler and T. W. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).

(10) NOTE ADDED IN PROOF. S. Takahashi, T. Shibano, and N. Hagihara, [*Tetrahedron Letters*, 2451 (1967)] have reported preliminary results related to ours on the preparation of alkoxyoctadienes and 1,3,7-octatriene.

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Received September 5, 1967

Reaction of Tertiary Nitriles with Solvated Electrons

Sir:

In a study of the conversion of dehydroabietonitrile (**1**) to tricyclic steroid analogs[1] of possible physiological activity, numerous routes were explored. It is the purpose of this communication to report on one, which involves the reductive decyanation of dehydroabietonitrile (**1**), to prepare the new compound dehydroabietene ($\Delta^{5,7,14(13)}$-abietatriene,[2] **4**) by solvated electrons in nearly quantitative yield.

Dehydrocyanation[3] of 2,2,3,3-tetraphenylpropionitrile by potassium amide in liquid ammonia by an E2 reaction, as well as decyanation[4] of trisubstituted acetonitriles by sodium amide in boiling aromatic solvents, has been noted. Repeated attempts were made to dehydrocyanate or decyanate **1** by sodium amide in liquid ammonia. In all instances only starting nitrile was recovered. However, interaction of dehydroabietonitrile with the solvated electrons of either sodium biphenyl radical anion or sodium in liquid ammonia afforded high yields of **4** (Scheme I). The products from the reaction of **1** with either one of these reagents

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(1) J. W. Huffman and P. G. Arapakos, *J. Org. Chem.*, **30**, 1604 (1965).

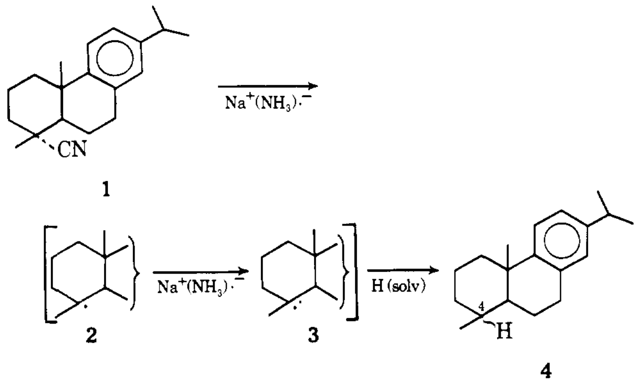
(2) J. Simonson and D. H. R. Barton, "The Terpenes," Vol. III, University Press, Cambridge, England, 1952, pp 391, 419.

(3) C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 82 (1956).

(4) A. W. Ruddy, *ibid.*, **73**, 4096 (1951); M. Jackman, F. C. Nachod, and S. Archer, *ibid.*, 72, 716 (1950); M. Jackman, C. Bolen, F. C. Nachod, B. F. Tullar, and S. Archer, *ibid.*, 71, 2301 (1949).

had the same yield and properties. It appears that the analytical procedure[5] for the quantitative determination of halides by the action of solvated electrons on organic halides also applied to organic nitriles (pseudo-halides).

Scheme I

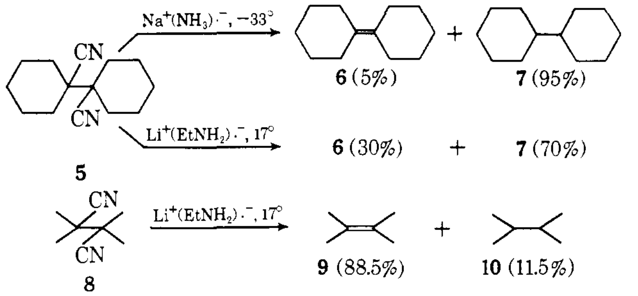


Dehydroabietonitrile[6] was added to sodium in liquid ammonia, and the solution was stirred at −78° for 2 hr and then at 25° until the ammonia evaporated. The blue color of the solvated electrons persisted throughout the entire stirring period. The resulting bluish gray residue was mixed with diethyl ether and then slowly hydrolyzed with water. The ether layer was removed and the remaining aqueous layer was washed thoroughly with more ether. The ether extracts afforded a colorless oil (95–97% yield) which according to its infrared spectrum was free of any starting nitrile:[7] $n^{27}\text{D}$ 1.53569; $[\alpha]^{25}\text{D}$ +71.7°; nmr ($CDCl_3$; cps) multiplet centered near 420, ArH; 168 (multiplet), >C*H*(CH_3); 71.5 (doublet), (CH_3)$_2$CH–; 64 (singlet), angular CH_3; 53.5 (doublet), C_4CH_3. Its mass spectrum was consistent with that expected for dehydroabietene[8] (**4**): a molecular ion at *m/e* 256 (calcd for **4**, 256) (21%) and abundant fragment ions at *m/e* 241 (100%), 185 (25%), and 159 (93%). *Anal.* Calcd for $C_{19}H_{28}$: C, 89.06; H, 10.94, Found: C, 89.18, H, 10.84. A vapor phase chromatogram (Carbowax 200°) of this product exhibited two peaks[9a] in the ratio of 13:1 at retention times of 16.1 and 18.4 min. From the reduction of $\Delta^{4\text{-}exo}$-abietanes which undergo α hydrogenations[9b] it would seem that the major and minor fractions would correspond to the β and α stereoisomers, respectively. The α isomer could conceivably arise from epimerization at the C_4 center through the intermediate **3**, in Scheme I.

The mechanistic justification shown in Scheme I is suggested by some recent work on electron-transfer reaction of radical anions with organic halides.[10] A stepwise two-electron transfer to **1** with initial cyanide loss could lead to carbanion **3** *via* the free radical **2**. Ultimate proton abstraction from the solvent could produce dehydroabietene (**4**). The conversion of **2** directly to **4** by combination with a hydrogen atom is improbable since, in the case of cholesteryl and cyclocholestanyl chlorides, the product is apparently independent of "the hydrogen-atom donor ability of the medium."[10b]

Next 1,1′-dicyanobicyclohexyl[11] and tetramethylsuccinonitrile[11] were allowed to react with solvated electrons as a possible one-step synthesis to the appropriate corresponding olefin (see Scheme II).

Scheme II



Accordingly, 1,1′-dicyanobicyclohexyl was allowed to react and the reaction products were characterized as described for dehydroabietonitrile. Spectral data (infrared and nmr)[7] proved that the resulting colorless hydrocarbon liquid (yield 95–98%) was principally bicyclohexane (**7**; 95%). Mass spectrometric analysis of this product further detected lesser amounts (5%) of bicyclohexylidene (**6**).

Shorter reaction times through the use of lithium in ethylamine were sought. Thus, the reaction of **5** with lithium in ethylamine for 10 min gave a colorless liquid (yield, 94–96%), again free of starting dinitrile, which proved to be a mixture of approximately 70% **7** and 30% **6**. This composition was based on the relative intensities of the molecular ion peaks at *m/e* 166 and 164, respectively,[12] as well as on direct comparison of **7** with an authentic sample.

Tetramethylsuccinonitrile (**8**) was similarly caused to react with lithium in ethylamine and the products were separated by vapor phase chromatography on Poropak Q at 150° The chromatogram obtained exhibited two peaks in the ratio of 1:7.7 at retention times of 11.2 and 13.2 min. Mass spectral analysis[13] of each of the peaks identified them as those for 2,3-dimethylbutane (molecular ion *m/e* 86) and 2,3-dimethyl-2-butene (molecular ion *m/e* 84), respectively.[14]

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(5) J. C. Bergmann and J. Savik, Jr., *Anal. Chem.*, **29**, 241 (1957); L. M. Liggett, *ibid.*, **26**, 748 (1954).

(6) The author thanks Dr. T. F. Sanderson of Hercules Powder Co. for the generous gift of dehydroabietonitrile.

(7) Infrared spectra were obtained on a P.E. 137 spectrophotometer, while molecular weight was determined from MS-9 mass spectrometric data. Proton magnetic resonance spectra were obtained on an A-60 with TMS as internal standard. Analytical gas chromatograms were obtained on a Varian Aerograph 202 with a thermal conductivity detector and an Aerograph Hy-Fi (A-600-D) gas chromatograph equipped with a hydrogen flame detector. Columns employed were 0.25 in. × 10 ft 10% CW 20 M TPA on 60–80 mesh Chromosorb W and 0.3 in. × 6 ft stainless steel Poropak Q 60–100 mesh. Rotations were determined on 1% solutions in chloroform with a Zeiss circle polarimeter 0.01.

(8) R. Ryhage and C. R. Enzell, *Arkiv Kemi*, **26**, 425 (1957); C. A. Geuge, *Anal. Chem.*, **31**, 1750 (1959).

(9) (a) Work for determining their stereochemistry is presently in progress. (b) A. W. Burgstahler and J. N. Marx, *Tetrahedron Letters*, 3333 (1964); N. P. Jensen and W. S. Johnson, *J. Org. Chem.*, **32**, 2045 (1967).

(10) (a) J. F. Garst, D. W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88**, 4260 (1966); (b) S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4262 (1966).

(11) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *ibid.*, **71**, 2661 (1949); C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951).

(12) "API Catalog of Selected Mass Spectral Data," American Petroleum Institute, Pittsburgh, Pa., 1961, Spectra No. 1288, 1508, and 1676.

(13) The mass spectra were obtained directly on the gas chromatograph effluent peaks by means of a coupled gas chromatograph–mass spectrometer system.

(14) API collection of uncertified mass spectra, no. 13, 15, 424, and 525.

A study is in progress[15] to define more completely the scope and breadth of these reactions.

Acknowledgment. The author thanks the Pioneering Research Fund of Battelle Memorial Institute for financial support of this investigation, Dr. R. L. Foltz and Mr. T. F. Page, Jr., for the mass spectrometric and nmr analyses, respectively, Mr. R. H. Poirier, Dr. G. A. Lutz, and Dr. H. M. Grotta for their helpful suggestions, and Professor J. Hine for his instructive comments.

[15] Nitriles other than *t*-nitriles that have been found to undergo this reaction as well as the analytical procedure for the *t*-nitriles will soon be published.

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Stereochemically Nonrigid Organometallic Molecules. IX.[1] Some Fluxional and Some Nonfluxional Compounds Derived from Cyclooctatetraene and Ruthenium Carbonyl

Sir:

Previous investigations of the reactions of the iron carbonyls with cyclooctatetraene (COT)[2] and its derivatives[3] have provided many interesting compounds, not all of which have been fully characterized as to structure and the nature of the fluxional processes operative in some of them. We have investigated the reaction of Ru$_3$(CO)$_{12}$ with C$_8$H$_8$ hoping to obtain analogs to some of the iron compounds which might lend themselves more readily to answering the major questions regarding structure and fluxional behavior.

The general preparative procedure for all compounds reported here is to reflux a hydrocarbon (generally heptane or octane) solution of Ru$_3$(CO)$_{12}$ and C$_8$H$_8$ and to separate and purify the products by suitable combinations of chromatography, sublimation, and recrystallization. Thus the following major[4,5] products have been isolated and characterized.[6]

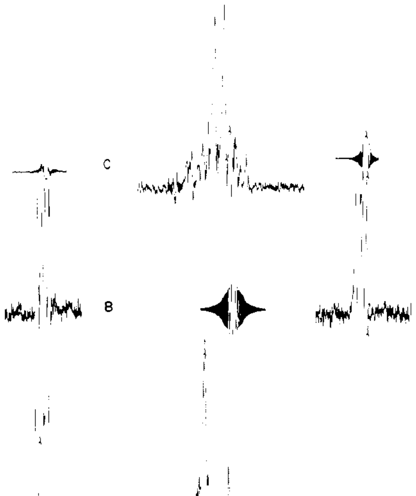

Figure 1. (A) The nmr spectrum of III (C$_6$H$_{12}$ solution, 35°). Line positions and intensities are τ 4.19 (2), $\sim$5.7 (4), 7.37 (2). (B) The spectrum when the central multiplet is irradiated. (C) The spectrum when the low- and high-field resonances are simultaneously irradiated.

I. (C$_8$H$_8$)Ru(CO)$_3$. The isolation of this substance has already been reported by ourselves[7] and others.[8] A thorough study of its nmr spectrum down to -147° coupled with the use of computer-simulated spectra for various models of the intramolecular rearrangement process responsible for its fluxional behavior have enabled us to specify the instantaneous configuration (1,3-diene to metal bonding) and the mechanism of rearrangement (1,2 shifts) with great certainty.[7] The orange crystalline C$_8$H$_8$Ru(CO)$_3$ (mp 75–76°) can be readily sublimed at 47° (0.05 mm). A determination of the unit cell and space group suggests that it is isostructural with (C$_8$H$_8$)Fe(CO)$_3$.[5,9] The mass spectrum is consistent with the assigned structure, and the ir spectrum is similar to that of C$_8$H$_8$Fe(CO)$_3$ (strong peaks in heptane at 2070, 2010, and 1996 cm^{-1}).

II. (C$_8$H$_8$)Ru$_2$(CO)$_6$. The molecular formula of this yellow crystalline substance (mp 90–95° dec) has been confirmed by X-ray crystallographic data.[10] The infrared spectrum in the CO stretching region is complex (in heptane, 2078, 2048, 2011, 2006 sh, 1988, and 1978 sh cm^{-1}); there are no bridging peaks. The nmr spectrum is shown in Figure 1a and is very similar to that reported by Pettit[2b] for a compound (C$_8$H$_8$)$_2$Fe$_2$(CO)$_6$ (designated in ref 2b as compound III) which suggests that the two compounds are isostructural. The analysis of this complex spectrum is considerably simplified by spin decoupling. Irradiation of the central multiplet (Figure 1b) removes the strong coupling of these protons to the high-field resonance which collapses to one-half of an A$_2$X$_2$ spectrum,[11] in which there is appreciable A–X coupling. Simultaneous irradiation of the high- and low-field multiplets (Figure 1c) removes their coupling to the protons of the central multiplet which simplifies to a typical A$_2$B$_2$ spectrum.[11]

These data indicate a structure in which the Ru$_2$(CO)$_6$ moiety is bonded to a sequence of carbon atoms in the carbocyclic ring (which has a free olefinic group, the protons of which give a resonance at τ 4.19) so as to permit a mirror plane which divides the eight ring protons into four equivalent sets (A$_2$B$_2$C$_2$X$_2$). The resonance of the protons at the extremities of the metal-bonded fragment occur at τ 7.37, while those of the central protons account for complex resonance at τ $\sim$5.7. Details of the geometry and bonding will be presented on completion of the X-ray study now in progress.[11a] Heating the complex in solution causes

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[1] Part VIII: F. A. Cotton, A. Musco, and G. Yagupsky, *J. Am. Chem. Soc.*, **89**, 6136 (1967).

[2] (a) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 366 (1960); (b) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

[3] (a) F. A. L. Anet, *ibid.*, **89**, 2491 (1967); (b) F. A. Cotton and A. Musco, *ibid.*, in press.

[4] At least two other compounds have been isolated in trace amounts. One appears to be the (C$_8$H$_8$)Ru$_2$(CO)$_6$ analog of the *trans*-(C$_8$H$_8$)Fe$_2$(CO)$_6$ compound[2a,5] (ir: 2067, 2000, 1992 (sh) cm^{-1}, all strong, heptane solution).

[5] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 37, 2084 (1962).

[6] All compounds had satisfactory C and H analyses; all ir frequencies are ± 5 cm^{-1}.

[7] W. K. Bratton, F. A. Cotton A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

[8] M. I. Bruce, M. Cooke, M. Green, and F. G. A. Stone, *Chem. Commun.*, 523 (1967).

[9] We thank Dr. Roger Eiss for crystallographic data on C$_8$H$_8$Ru(CO)$_3$.

[10] We are indebted to Mr. W. T. Edwards for this determination.

[11] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).