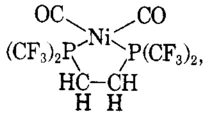
## A Volatile Chelated-Nickel Dicarbonyl[1]

*Sir:*

Chelation of nickel by bis-phosphines or bis-arsines, forming heterocyclonickel dicarbonyls, has been accomplished by Chatt and Hart[2]; however, no compound in this class was reported to be volatile without decomposition, whereas volatility often would be advantageous for the further study of such substances. Accordingly, we have used high-vacuum methods to make the study of a new volatile compound presumed to have the structure



hereinafter designated as "D." D was attacked by $PF_3$ to form another volatile derivative of the same ring, with comparable small yields of the known $(PF_3)_2Ni(CO)_2$ and $(PF_3)_3NiCO$, and major yields of nonvolatiles having infrared bands for Ni–CO–Ni bridging.

**Synthesis.**—An equimolar mixture of $Ni(CO)_4$ and the bis-phosphine $(CF_3)_2PC_2H_4P(CF_3)_2$[3] (hereinafter designated as "B") liberated CO bubbles immediately upon warming to 25° and was allowed to stand for a few days to complete the process. However, the yield of D was only 25%; repetition at 40° gave only an 8% yield. Actually, a polymer might be expected if some units encounter others faster than each can cyclize. Dilution favors single-unit cyclization; thus in benzene under dry nitrogen at 60° the yield rose to 50%, augmented further by boiling the benzene solution of the nonvolatile by-product. This was partly converted to the monomer in the manner of the presumed dimer $[(C_2H_5)_2PC_2H_4P(C_2H_5)_2Ni(CO)_2]_2$.[2]

**Physical Properties.**—The colorless crystals of D melted in the range 4.5–6.0°. Its molecular weight (vapor, 8 mm. and 90°) was 485 (calcd. 481). Its regionally averaged vapor tensions (Table I) agree with an equation from which $\Delta S_{\text{vap}} = 21.00$ e.u. and b.p. 203°, suggesting acceptable purity.

TABLE I

VAPOR TENSIONS OF $(CF_3)_2PC_2H_4P(CF_3)_2Ni(CO)_2$

($\log P_{\text{mm.}} = 6.6902 + 1.75 \log T - 0.004912\, T - 2931/T$)

| $t$, °C. | 30.0 | 36.3 | 41.2 | 46.3 | 51.2 | 60.4 |
|---|---|---|---|---|---|---|
| $P$mm. (obsd.) | 0.75 | 1.13 | 1.56 | 2.14 | 2.82 | 4.82 |
| $P$mm. (calcd.) | 0.75 | 1.14 | 1.56 | 2.13 | 2.86 | 4.79 |

**Chemical Behavior.**—D decomposes slowly to CO and nonvolatiles at 70°, so that physical measurements at higher temperatures must be made rapidly. Its reaction with iodine in $CCl_4$ at 25° yielded all of the CO (11.5% by wt.; calcd. 11.6%); then nickel was determined as 12.0% (calcd. 12.2%) by the dimethylglyoxime method. The B content is estimated by difference as 76.5% (calcd. 76.2%). Its major presence in the $CCl_4$ solution was confirmed by its infrared spectrum. With the molecular weight, these results prove the formula of D.

One D with 10 $PF_3$, in a closed tube at 70°, consumed 1.81 $PF_3$ during 18 days, liberating an unmeasured amount of CO. One fraction of the product (trapped *in vacuo* at −120° to remove $PF_3$) showed infrared peaks at 2085, 2102, and 2064 cm.$^{-1}$, as reported for $(PF_3)_3NiCO$ (2082) and for $(PF_3)_2Ni(CO)_2$ (2099 and 2061).[4] The P–F stretching bands appeared at 931, 903, and 864 cm.$^{-1}$. A less volatile fraction, not easily separable from D, showed (by the Infracord instrument) a single C–O stretching band at 2066, one P–F band at 883 cm.$^{-1}$, and C–F stretching just like that of D. The formula $(CF_3)_2PC_2H_4P(CF_3)_2NiPF_3CO$ seems probable.

The major D–$PF_3$ reaction product was a nonvolatile oil showing C–H stretching (Infracord) at 2933, C–O stretching at 2053, typical C–F and P–F stretchings, and a strong peak at 1727 cm.$^{-1}$, indicating Ni–Co–Ni bridging. A nonvolatile white-solid final product has not been examined.

Triphenylphosphine (large excess) also attacked D, liberating 30% of its CO during 12 hr. in benzene at 70°. Some of the ligand B also was displaced; there was no other volatile product. The benzene solution of the nonvolatiles showed C–O absorption at 2016 and 1946 cm.$^{-1}$ and a C–F stretching spectrum just like that of D.

**Infrared Study of D and B.**—The infrared spectra of the vapors of D and B were compared, using path lengths near 100 mm. and respective pressures of 1.44 and 18 mm. The relative intensity of each band maximum was calculated as $k = (100/PL) \log I_0/I$ (path $L$ and pressure $P$ both in cm.) and shown in parentheses after the frequency in cm.$^{-1}$; however, very intense bands had to be recorded at unknown pressures too low for useful calculations of intensity.

Bands unique for D are C–O stretchings 2090 (vvs), 2057 (vvs), and 2018 (4.9); and ring-$CH_2$ motions 1089 (4.9) and 1054 (1.5). B showed C–H stretchings 2984 (0.03), 2961 (0.02), 2941 (0.05), 2931 (0.04), 2854 (0.10), 2730 (0.05); and C–F stretching overtones appeared at 2290 (0.7), 2256 (0.4), 2244 (0.4). For D the pressure was too low to show any of these modes.

Corresponding bands for D and B are the $CH_2$ deformations D1420 (2.4) *vs.* B1431 (1.6) and D1310 (5.1), 1259 (3.5) *vs.* B1282 (1.9); C–F stretchings D1195, 1174, 1158, 1122 *vs.* B1197, 1169, 1147, 1114 (all vvs); $CH_2$ motions D878 (3.8), 811 (4.6) *vs.* B877 (0.3), 797 (0.1); $CF_3$ asymmetrical deformation D734 (21) *vs.* B748 (1.0), 726 (0.8); P–$CH_2$ stretchings D683 (2.4), 655 (2.3) *vs.* B691 (1.3), 657 (0.3); $CF_3$ symmetrical deformation D562 (3.2) *vs.* B558 (2.3); and P–$CF_3$ stretchings D481 (13) *vs.* B486 (1.0). Bands D534 (11), D522 (2.4), and B542 (0.7) might correspond, but D507 (3.8), 506 (5.4) are not easily assigned. Also uncertain of assignment are D464 (18), 437 (6.4), 399 (4.6), and B446 (4.0), 444 (4.0), 361 (3.0), 1889 (0.7), 1853 (0.2).

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[1] It is a pleasure to acknowledge the support of this research through National Science Foundation Grant No. GP-199. Except as otherwise specified, all infrared spectra were recorded within 1 cm.$^{-1}$ by a Beckman IR7 spectrophotometer with NaCl and CsI optics, provided by National Science Foundation Grants G-14465 and GP-199.

[2] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[3] First made by L. R. Grant, Ph.D. Dissertation, University of Southern California Libraries, 1960; *cf.* also A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961).

[4] M. Bigorgne and A. Zelner, *Bull. soc. chim. France*, 1986 (1960).

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## Alkylidenecarbenes[1]

*Sir:*

The addition of carbenes to olefins is used as a criterion to establish the intermediate formation of these reactive species.[2] When 1-chloro-2-methylpropene-1 (I, 0.25 mole) was treated with potassium *t*-butoxide

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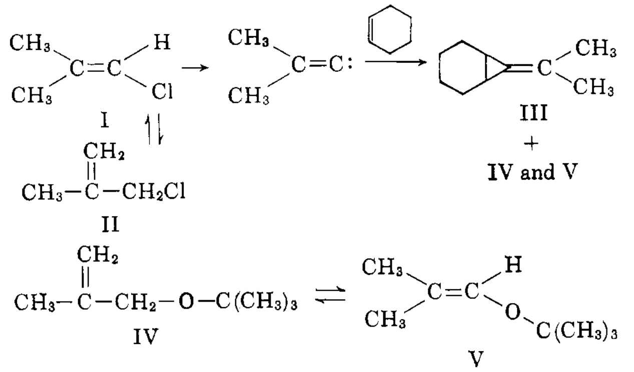
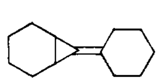
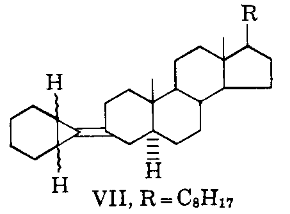
[1] This investigation was supported by Public Health Service Research Grant AM-05183 from the National Institute of Arthritis and Metabolic Diseases.

[2] (a) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6182 (1954); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) H. O. Hartzler, *ibid.*, **83**, 4990 (1961).

(0.30 mole) in 370 ml. of boiling tetrahydrofuran for 16 hr. in the presence of an excess of cyclohexene (0.95 mole), 7-isopropylidenenorcarane (III) was isolated (8%),[3] indicating the intermediate formation of isopropylidenecarbene.




VI


VII, R = $C_8H_{17}$

The carbene adduct III in the n.m.r. spectrum shows the allylic methyl group signals at 8.25 τ,[4] mol. wt. 136 (mass spec.), infrared 5.63 $\mu$ (>C=C<), $n^{24}\text{D}$ 1.4753.

In addition to the isopropylidene carbene adduct III, a mixture of isomeric *t*-butyl ethers, 1-*t*-butoxy-2-methylpropene-2 (IV) and 1-*t*-butoxy-2-methylpropene-1 (V), was isolated. This mixture of ethers could not be adequately resolved by gas chromatography, but an n.m.r. spectrum of the mixture indicated the composition of IV to V as (3:1).

Reaction of the isomeric allylic chloride 1-chloro-2-methylpropene-2 (II) with potassium *t*-butoxide in tetrahydrofuran in the presence of excess cyclohexene led unexpectedly to the same 7-isopropylidenenorcarane adduct (III) (20%) and about the same composition of isomeric ethers IV and V was isolated as obtained from the vinylic isomer 1-chloro-2-methylpropene-1 (I).

These results indicate that interconversion of the allylic and vinylic chlorides occurs under these reaction conditions and the isopropylidenecarbene is generated by 1,1 elimination from the vinylic chloride. The origin of the isomeric *t*-butoxy ethers is through the displacement reaction on the allylic chloride by *t*-butoxide ion. The allylic *t*-butyl ether formed in this manner is then isomerized to the vinylic *t*-butyl ether with potassium *t*-butoxide.[5]

In accord with this supposition, rapid quenching of a reaction mixture of 1-chloro-2-methylpropene-2 (II) and potassium *t*-butoxide in boiling toluene led to an isomeric chloride mixture of I and II of (1:1.25) by analysis of the n.m.r. spectrum.

Other alkylidenecarbenes were generated by treatment of the appropriate chloride and captured as the cyclohexene adduct. Chloromethylenecyclohexane[6] yielded the cyclohexylidenecarbene adduct VI, mol. wt. 176 (mass spec.), infrared 5.62 $\mu$ >C=C<, $n^{25}\text{D}$ 1.5070. This carbene adduct VI was accompanied by *t*-butoxymethylenecyclohexane.[7]

A steroidal vinylic chloride, 3-chloromethylenecholestane, m.p. 80–81°, $[\alpha]\text{D}$ +21°, yielded the carbene adduct VII (25%),[8] m.p. 160–163°, $[\alpha]\text{D}$ +27°, mol. wt., 482, infrared 5.62 $\mu$ (>C=C<). Also isolated from the reaction was 3-*t*-butoxymethylenecholestane, m.p. 104–106°, $[\alpha]\text{D}$ +26°.

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(3) Satisfactory analyses have been obtained for all new compounds reported herein. Rotations are reported in chloroform.

(4) Splitting of the methyl groups signals is apparent in the n.m.r. spectrum of III, this effect is either due to the nonequivalence of the methyl groups in different conformational environments or a long-range spin–spin coupling effect. This problem is under further study.

(5) (a) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961); (b) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961). The facile isomerization of allyl ethers to vinyl ethers in the presence of potassium *t*-butoxide is reported by these authors.

(6) These chloromethylene derivatives are conveniently prepared by the Wittig reaction of chloromethyltriphenylphosphonium chloride and ketones by the method of D. Seyferth, S. O. Grim, and T. O. Read, *ibid.*, **83**, 1617 (1961).

(7) It is of interest that treatment of chloromethylenecyclopentane with potassium *t*-butoxide in toluene in the presence of cyclohexene yielded no products of cyclopentylidenecarbene addition to cyclohexene. The only product isolated was 1-*t*-butoxymethylcyclopentene. This finding is in accord with the report [A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962)] that methylenecyclopentane is more rapidly converted to the endocyclic isomer than methylenecyclohexane. The rapid isomerization of chloromethylenecyclopentane to the endocyclic allylic chloride followed by chloride displacement with *t*-butoxide ion seems to be a plausible explanation for the apparent absence of carbene product in this reaction.

(8) Thin layer chromatography of this material showed the persistant presence of two closely migrating spots. This material is presumably a mixture of $\alpha$- and $\beta$-isomers of the norcarane ring system.

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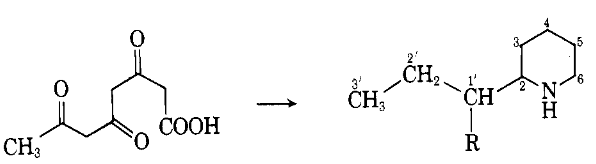
## The Biosynthesis of Coniine from Four Acetate Units[1]

*Sir:*

It has been generally accepted that coniine (II, R = H), one of the alkaloids found in hemlock (*Conium maculatum*), is produced in the plant by a condensation between $\Delta^1$-piperideine (derived from lysine) and acetoacetic acid followed by unexceptional decarboxylation and reduction.[2] Some tracer work has been reported[3] which apparently substantiated this hypothesis. Uniformly labeled L-lysine-$C^{14}$ was fed to *C. maculatum* and radioactive coniine isolated from the plants several days later. However the alkaloid was not degraded to determine the distribution of activity.

Some seven years ago we fed DL-lysine-2-$C^{14}$ to hemlock plants by adding the tracer to a hydroponic solution in which the roots were growing. The crude alkaloids isolated from the plant had very low activity. A similar result was obtained when cadaverine-1,5-$C^{14}$ was fed to the plants.[4] More recently a solution of lysine-2-$C^{14}$ was administered to hemlock plants, growing in soil, by means of a cotton wick inserted into the stem. Again, alkaloids of very low activity were obtained. We therefore proposed an alternate hypothesis for the biosynthesis of coniine and related piperidine



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(1) This investigation was supported by research grant GB-363 from the National Science Foundation.

(2) R. Robinson, "The Structural Relations of Natural Products," Clarendon Press, Oxford, 1955.

(3) U. Schiedt and H. G. Höss, *Z. Naturforsch.*, **13b**, 691 (1958); *Z. physiol. Chem.*, **330**, 74 (1962).

(4) Cadaverine-1,5-$C^{14}$ was a much more efficient precursor of the piperidine ring of anabasine than lysine-2-$C^{14}$; E. Leete, *J. Am. Chem. Soc.*, **80**, 4393 (1958).