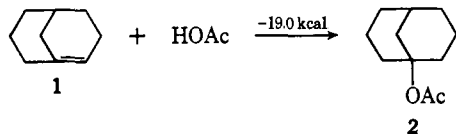


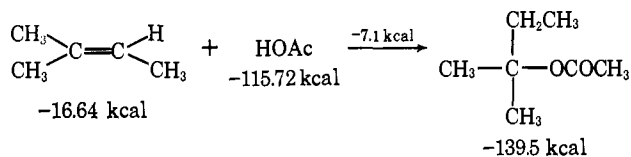
nmr spectral properties of a mixture of pure **2** and acetic acid with those of a solution of **1** in 264 mg



of acetic acid which had been allowed to stand over night at room temperature in an evacuated ampoule.

The enthalpy change for the transformation olefin (liquid) + acetic acid (liquid) → acetate (solution) is  $-18.51 \pm 0.35$  kcal/mol at  $25^\circ$ .<sup>6</sup> Correction of this figure for the heat of solution<sup>6</sup> of **2** in acetic acid (0.48 kcal/mol) gives a value of  $-19.0$  kcal/mol for the heat of reaction with all components in the liquid state.

For purposes of comparison we have estimated the heat of reaction for the model transformation



under the same conditions of state. Unfortunately, reliable modern data on the heats of formation of acetate esters are not extensive, and in no case of which we are aware has the heat of formation of a tertiary acetate been determined. The calculation was therefore carried out as follows.

The heat of formation of 2-methylbutene-2 in the liquid phase at  $25^\circ$  ( $-16.64$  kcal/mol) was obtained from the gas-phase value ( $-10.17$  kcal/mol)<sup>7</sup> and the known heat of vaporization (6.47 kcal/mol).<sup>7</sup> The figure of  $-115.72$  kcal/mol employed for the heat of formation of liquid acetic acid ( $25^\circ$ ) is that of Evans and Skinner.<sup>8</sup>

A value of  $-1000.4$  kcal/mol has been reported for the heat of combustion of liquid isoamyl acetate at  $20^\circ$  by Schjanberg.<sup>9</sup> The heat of formation of liquid isoamyl acetate is thus  $-136.19$  kcal/mol. This figure is corrected to one for *t*-amyl acetate by application of Franklin's gas-phase group equivalents<sup>10</sup> with the proviso that the heats of vaporization of isoamyl acetate and of *t*-amyl acetate do not differ materially (*cf.* Trouton's rule). Thus the Franklin gas-phase heats of formation ( $25^\circ$ ) of the isoamyl and *t*-amyl groups are, respectively,  $-31.18$  and  $-34.49$  kcal, the difference being  $-3.31$  kcal. The heat of formation of liquid *t*-amyl acetate is thus calculated to be approximately  $-139.5$  kcal/mol and is to be regarded as an essentially strain-free value.<sup>11</sup>

(6) The colorimeter employed in this work has been described previously [R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957)]. Acetic acid (225 ml) was employed as solvent with olefin samples in the range 225–400 mg.

(7) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1954.

(8) F. W. Evans and H. A. Skinner, *Trans. Faraday Soc.*, **55**, 260 (1959).

(9) E. Schjanberg, *Z. Physik. Chem.*, **A172**, 197 (1935).

(10) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(11) Alternatively the heat of formation of *t*-amyl acetate can be calculated as the sum of Franklin group equivalents (4 CH<sub>3</sub>,  $-40.48$  kcal; CH<sub>2</sub>,  $-4.926$  kcal; C,  $+0.8$  kcal; ester carboxylate,  $-79.8$  kcal) and is  $-124.41$  kcal/mol for the gas phase at  $25^\circ$ . Correction for the heat of vaporization, for which the isoamyl acetate value of 9.0 kcal/mol<sup>9</sup> is the only experimental one available (the Trouton rule figure

The heat change for the model reaction derived from this result is  $-7.1$  kcal/mol. If the validity of this figure is assumed, then the strain associated with the double bond in bicyclo[3.3.1]non-1-ene (**1**) is about 12 kcal/mol.<sup>12</sup> Although this is the lowest of the values that can be calculated from currently available data,<sup>11</sup> we believe that it is based upon the most reliable experimental source. This degree of strain is of the same order of magnitude as that found in *trans*-cyclooctene (9.2 kcal/mol)<sup>13</sup> and in *cis*-di-*t*-butylethylene (9.3 kcal/mol)<sup>14</sup> and is substantially less than the double bond strain of about 20 kcal/mol found in dimethylcyclopentene.<sup>15</sup> The result is surprisingly low in view of the extreme reactivity of bicyclo[3.3.1]non-1-ene toward addition of acetic acid.

for *t*-amyl acetate is 8.74 kcal/mol), gives a final liquid phase heat of formation of  $-133.41$  kcal/mol. It should be noted that the Franklin ester carboxylate group equivalent is based upon a 1928 International Critical Tables heat of formation of ethyl acetate. The value of  $-133.41$  kcal/mol can be revised upward to  $-131.88$  or downward to  $-135.02$  kcal/mol if more recent data for ethyl acetate are employed [ref 9 and A. A. Vvedenskii, P. Ya. Ivannikov, and V. A. Nekrasova, *Zh. Obshch. Khim.*, **19**, 1094 (1949)].

(12) Implicit in this argument is the assumption that residual strains in **1** and in **2**, if significant, are at least comparable. This assumption is supported in some degree by the fact that the heat of hydrogenation of bicyclo[3.2.1]oct-2-ene ( $-26.8$  kcal/mol) is normal and close to that of cyclohexene ( $-27.1$  kcal/mol) (unpublished results of B. J. Mallon and R. B. Turner).

(13) R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

(14) R. B. Turner, D. E. Nettleton, and M. Perelman, *ibid.*, **80**, 1430 (1958).

(15) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

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### Oxidation and Isomerization of Phenylcyclopropane by Aqueous Palladium(II) Chloride<sup>1</sup>

Sir:

While the literature is replete with accounts of the addition of platinum(II) to olefins, the analogous reaction of the transition metal ion with cyclopropanes is almost without precedent. Cyclopropane is reported to cleave in the presence of platinum(II) to yield a complex with an incorporated trimethylene bridge as a bidentate ligand.<sup>2</sup> Recently cyclopropane-platinum chloride complexes, formed by ligand exchange with olefin-platinum chloride complexes, have been reported.<sup>3</sup>

Palladium(II) is postulated to provide a transient complex ion in aqueous solutions of olefins, which then undergoes an internal redox reaction, involving a 1,2-hydride shift, to produce carbonyl products.<sup>4</sup> There are no reports of a corresponding reaction of palladium(II) with cyclopropanes. While the cleavage reaction certainly would be expected to occur, the products are not predictable *a priori*. An intermediate

(1) This research was supported by Grant GP3873 from the National Science Foundation.

(2) P. I. Adams, J. Chatt, R. Guy, and N. Sheppard, *Proc. Chem. Soc.*, 179 (1960); *J. Chem. Soc.*, 738 (1961).

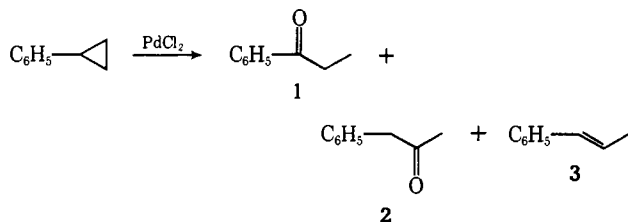
(3) W. J. Irwin and F. J. McQuillin, *Tetrahedron Letters*, 1937 (1968).

(4) P. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964); J. Smidt, *Angew. Chem. Intern. Ed. Engl.*, **1**, 80, 1962; A. Aguiló, *Advan. Organometal. Chem.*, **5**, 321 (1967); C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London, 1967, pp 117–148.

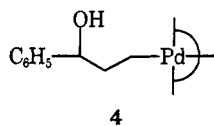
analogous to the proposed olefin intermediate would have to undergo a 1,3-hydride shift in order to produce ketonic products. However, other mechanistic pathways may be available for such an intermediate.

The conditions for the conversion of phenylcyclopropane into the observed products by palladium(II) chloride involve aqueous solutions at 75°. Only the reaction times and the molar ratio of phenylcyclopropane to the palladium(II) chloride will be given in this report. All products in this remarkably clean reaction system were characterized by their nmr spectra. The reported yields are based on nmr integration in order to avoid isomerization, condensation, and polymerization complications that can occur under vpc analytical conditions. The products were collected from vpc columns for identification purposes only.

Phenylcyclopropane and palladium(II) chloride in a 1:1 ratio react in 2 hr to produce propiophenone (1) and phenylacetone (2) in 60 and 35% yields, respectively. The remaining organic material consists of unreacted phenylcyclopropane and *trans*-propenylbenzene (3), indicating that the oxidation reaction is essentially quantitative. The origin of propiophenone is most



reasonably rationalized by the intermediacy of a Markovnikov-type adduct (4) which is a homolog of the adduct postulated for olefin reactions. The palladium



adduct apparently can transfer a hydride ion from the benzyl carbon to the terminal position of the chain with concomitant loss of neutral palladium. Use of D<sub>2</sub>O as solvent does not lead to incorporation of deuterium into the methyl group. Therefore propiophenone does not arise from protolysis of the intermediate to yield 1-phenyl-1-propanol which could then be oxidized.<sup>5</sup> Propiophenone is not derived from loss of elemental palladium and HCl to form 1-phenylallyl alcohol. The unsaturated alcohol is not converted into propiophenone by elemental palladium or palladium(II) chloride. In fact it is converted into an extremely complex mixture of substances, the nmr spectrum of which is not identical with the reaction products of the cyclopropane reaction. The products of the cleavage of phenylcyclopropane were monitored as a function of time, and these studies did not yield any evidence of organic substances other than those in the final reaction mixture.

The derivation of the unexpected product, phenylacetone, *via* a direct route from phenylcyclopropane is very unlikely. The presence of a small quantity of the isomeric *trans*-propenylbenzene suggests that it is the

(5) W. G. Lloyd, *J. Org. Chem.*, **32**, 2816 (1967).

precursor from which phenylacetone is produced. Such a route requires an anti-Markovnikov addition. However, *trans*-propenylbenzene does react under the same reaction conditions as employed for cyclopropane oxidation to produce phenylacetone exclusively.

Allylbenzene reacts with palladium(II) chloride to yield the expected Markovnikov-type product, phenylacetone. However, *trans*-propenylbenzene is produced in the reaction, suggesting that isomerization can occur readily, and, therefore, consequently providing supporting precedent for the isomerization process in the case of phenylcyclopropane. Allylbenzene could be the precursor which gives rise to phenylacetone in the cyclopropane reaction, although we regard this as more unlikely than the direct isomerization of phenylcyclopropane to *trans*-propenylbenzene.

In order to produce both propiophenone and phenylacetone in the cyclopropane oxidative cleavage and isomerization reaction, certain kinetic requirements must be met. The rate of isomerization must be of comparable magnitude to the oxidation reaction, and the relative reactivities of phenylcyclopropane and *trans*-propenylbenzene must be similar. The latter criterion has been shown to be met by an experiment in which phenylcyclopropane, *trans*-propenylbenzene, and palladium(II) chloride in the ratio 1:1:2 are allowed to react. After 2 hr the quantities of the two substrates remaining were nearly in a 1:1 molar ratio.<sup>6</sup>

A clue to the nature of the isomerization process and substantiation of the first kinetic requirement (*vide supra*) is provided by reactions in which the phenylcyclopropane is present in excess. When the ratio of phenylcyclopropane to palladium(II) chloride is 4:1, the apparent course of the reaction is dramatically altered. After 2 hr the only significant product (approximately 0.15 mole fraction of the organic material) formed is *trans*-propenylbenzene, although a detectable amount of propiophenone is present. However, after 26 hr both product ketones are present in addition to *trans*-propenylbenzene. The mole fraction of phenylcyclopropane converted to carbonyl compounds is approximately 0.25, as required by the oxidative capability of the palladium(II). However, the fraction of phenylcyclopropane converted to *trans*-propenylbenzene is also approximately 0.25. Accordingly, the isomerization process occurs in competition with the oxidation steps. No reaction occurs in the presence of palladium metal.

The apparent paradox of a slowing of the oxidation reaction with increasing quantities of the substrate and the conversion of substrate to products by both isomerization and oxidation steps may be the result of a multi-equilibrium system in which palladium(II) chloride may complex with either one or two cyclopropane molecules.<sup>7</sup> We speculate that coordinated water is necessary for propiophenone formation and that two cyclopropanes coordinated to palladium prevent this from

(6) A similar observation has been made in a comparison of the rates of oxidation of styrene and phenylcyclopropane by thallium(III) acetate. The rate of oxidation of styrene (G. Kordosky, M.S. Thesis, The Ohio State University) is only 10% larger than that of phenylcyclopropane (A. South Jr., Ph.D. Thesis, The Ohio State University).

(7) A referee has indicated that we in fact do not have any quantitative equilibrium data to support our postulated system of one or two cyclopropane molecules complexed to palladium(II). We agree, and only suggest this model as a working hypothesis. Kinetic and equilibrium data are currently being sought to further our knowledge of the mechanisms of the reactions herein reported.

occurring. In such a complex, a secondary process, namely isomerization to *trans*-propenylbenzene, occurs. The free olefin may compete for ligand positions in separate or mixed sets of complex ions. However, it is required that the nature of the olefin complex be different from that of the cyclopropane complex as the products of each reactant are different.

When the ratio of palladium(II) chloride to phenylcyclopropane is 4:1, the yield of propiophenone is approximately 95% after 2 hr. No phenylacetone or *trans*-propenylbenzene is observed. Therefore, the oxidative cleavage reaction of phenylcyclopropane is enhanced, and this fact is consistent with the expected mass law effect on the formation of a complex ion containing one cyclopropane moiety.

Studies of the effect of structure are being undertaken in addition to experiments designed to elucidate further the structures of postulated intermediates. Deuterium-labeling experiments are being carried out in order to determine the origin and ultimate destination of the postulated hydride shifts in both the oxidation and isomerization reaction.

(8) Sinclair Oil Fellow, 1967–1968.

Robert J. Ouellette, Charles Levin<sup>8</sup>

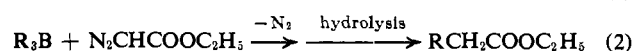
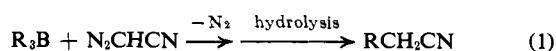
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### The Alkylation of Diazoacetone and Ethyl Diazoacetate by Means of Organoboranes. A New Synthesis of Nitriles and Esters

Sir:

We wish to report that trialkylboranes react with diazoacetone and ethyl diazoacetate, respectively, with expulsion of nitrogen and provide, after hydrolysis, novel and facile routes to the corresponding homologated nitriles (1) and ethyl esters<sup>1</sup> (2). In concert



with hydroboration, these reactions permit the over-all conversion of olefins into two-carbon-atom chain-extended derivatives possessing useful functionality.<sup>2</sup>

These reactions probably proceed by a mechanism analogous to that described earlier.<sup>2</sup> Both processes, however, occur with varying efficiency, and the following salient features have been noted.

**Nitriles.** The reactions of organoboranes derived from terminal olefins as well as cyclopentene proceed rapidly (as evidenced by complete nitrogen evolution) at ice-bath temperatures. Yields are excellent (93–100%). The product obtained from the organoborane derived from 1-hexene contained 95% octanenitrile and 5% 3-methylheptanenitrile. Since hydroboration of monosubstituted terminal olefins produces approximately 94% primary and 6% secondary alkyl groups,<sup>3</sup>

(1) For alternative ester syntheses based on organoborane homologation, see: J. J. Tufariello, L. T. C. Lee, and P. Wojtkowski, *J. Am. Chem. Soc.*, **89**, 6804 (1967); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).

(2) We have previously reported the functionalization of olefins into ketones via hydroboration; cf. J. Hooz and S. Linke, *ibid.*, **90**, 5936 (1968).

it is apparent that in this reaction the primary and secondary alkyl groups migrate with equal facility.

More sterically hindered trialkylboranes react somewhat more sluggishly and give lower yields.<sup>4</sup> The results are summarized in Table I. Moreover, that triarylboranes also undergo this reaction was demonstrated by the conversion of triphenylborane to phenylacetonitrile (52%).

Table I. Functionalization of Olefins into Nitriles by Reaction of the Corresponding Trialkylboranes<sup>a</sup> with Diazoacetone

Olefin	Product, <sup>b</sup> %	Yield, <sup>c</sup> %
1-Hexene	Octanenitrile, 95 3-Methylheptanenitrile, 5	100
1-Heptene	Nonanenitrile, 93 <sup>d</sup>	93
Cyclopentene	Cyclopentylacetonitrile	99
2-Methyl-1-pentene	4-Methylheptanenitrile	97
<i>trans</i> -3-Hexane <sup>e</sup>	3-Ethylhexanenitrile	54

<sup>a</sup> Hydroboration was conducted such that complete conversion to  $R_3B$  was ensured. <sup>b</sup> Structures were secured by direct comparison, comparison with literature constants, or acceptable compositional analyses and compatible spectral data. <sup>c</sup> By glpc analysis. Yield based on the utilization of one alkyl group of  $R_3B$ . A 50% excess of diazoacetone was employed although we have not yet determined that this amount is necessary. A 1:1 molar ratio gives somewhat lower yields. <sup>d</sup> Approximately 5% of another product, presumably 3-methyloctanenitrile, was also detected. <sup>e</sup> Reaction was conducted at 25° for 2 hr followed by a 4-hr reflux.

The method illustrated for the conversion of cyclopentene to cyclopentylacetonitrile is representative. To an ice-cooled, magnetically stirred solution of tri-cyclopentylborane (prepared in the usual manner<sup>3</sup> from cyclopentene (63 mmol) in 15 ml of tetrahydrofuran and a solution of borane (20 mmol) in tetrahydrofuran) was added a solution of diazoacetone (30 mmol) in 15 ml of tetrahydrofuran over a period of 30 min. The solution was stirred for 2 hr at room temperature and then cooled in an ice bath, and 25 ml of a 3 *N* potassium hydroxide solution<sup>6</sup> was added. The reaction mixture was stirred at room temperature an additional 0.5 hr. After the addition of brine solution, glpc analysis of the organic extract indicated a 99% yield of cyclopentylacetonitrile. Evaporation of solvent and distillation of the residue afforded 1.76 g (81%) of cyclopentylacetonitrile, bp 85–86° (16 mm).

**Esters.** As in the nitrile synthesis, organoboranes derived from 1-alkenes liberate nitrogen smoothly at ice-bath temperature on treatment with ethyl diazoacetate. However, the organoborane-diazoacetic ester reaction appears to be considerably more sensitive to steric factors, as evidenced by the variation of yield (40–83%) with olefin structure.<sup>4</sup> Moreover, the tri-

(3) (a) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963); (b) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(4) A side reaction takes place which consumes diazo compound. We are investigating this in greater detail in an attempt to circumvent this difficulty.

(5) **Caution!** Although no difficulties were ever encountered in numerous reactions of this substance with a variety of organoboranes, the isolation of this diazo compound is occasionally fraught with capricious explosions. It is recommended that adequate safety precautions be observed in preparing this material. Cf. S. H. Harper and K. C. Sleep, *J. Sci. Food Agr.*, **6**, 116 (1955), and T. Curtius, *Ber.*, **31**, 2489 (1898).

(6) Subsequent experiments have indicated that the intermediate  $\alpha$ -borylnitrile may be conveniently hydrolyzed by water in the absence of base, as described below for the ester synthesis.