126.00, 127.92, 128.03, 128.21, 128.69, 130.55, 140.34, 140.77, 176.53 (s). Anal. Calcd for $C_{19}H_{14}O_2$ (274.1): C, 83.19; H, 5.14. Found: C, 83.21; H, 5.10.

X-ray Crystallography of Urazoles 3b and 7 and Endoperoxides 8 and 12b. The crystals were optically centered on a Syntex $P\bar{1}$ four circle diffractometer. The intensities of all reflections were measured according to the ω technique (Mo Kα, graphite monochromator) using a scan range of 1° and a scan speed between 0.5 and 24.0 deg min^{-1} as a function of the intensities of the reflections. In the range between $3.0° \leq 2\theta \leq 55.0°$ all reflections hkl with $F > 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL System on an Eclipse S/250 at the Max-Planck-Institut für Festkörperforschung was employed. All structures were solved by the direct phase determination. The parameters of the complete structures could be refined by anisotropic least-squares cycles to the given R values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Special X-ray operations and results are listed in Table I, the positional and thermal parameters in Tables II–V, and the bond lengths and angles in Tables VI–IX, respectively (see supplementary material). We have omitted the presentation of the structure factors, which can be obtained upon request.

Acknowledgements are made to the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for generous financial support of this work. We thank Dr. D. Scheutzow (Würzburg) for running the NMR spectra, Prof. G. Maier's staff (Universität Giessen) for elemental analyses, Prof. F.-G. Klärner (Universität Bochum) for the high-resolution mass spectra, and Dr. G. Lange (Würzburg) for the regular mass spectra.

Registry No. **T-1a**, 36673-54-8; **T-1b**, 36673-53-7; **T-1c**, 36677-51-7; **T-1d**, 33604-51-2; **3a**, 82238-71-9; **3b**, 82238-72-0; **3c**, 82238-73-1; **6**, 82238-75-3; **7**, 88980-94-3; **8**, 82238-76-4; **9**, 88969-12-4; **10**, 88969-13-5; **11**, 82238-77-5; **12a**, 88969-14-6; **12b**, 89015-99-6; **13**, 88969-15-7; PTAD, 4233-33-4; MTAD, 13274-43-6; O_2, 7782-44-7.

Supplementary Material Available: Crystal data of **3b**, **7**, **8**, and **12b**, atomic coordinates, thermal parameters, bond lengths, and bond angles in Tables I–IX (9 pages). Ordering information is given on any current masthead page.

Structures of Pyridines Obtained in the Aluminum Bromide Mediated Cyclocongregation of Acetylenes with Cyanoformates

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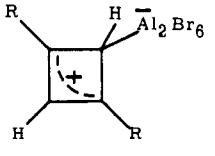
Received September 6, 1983

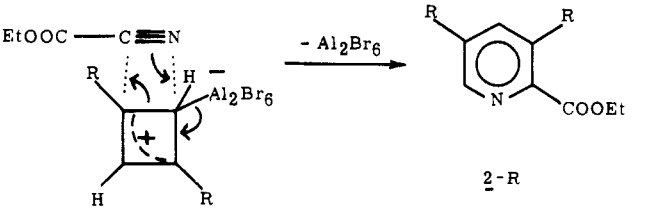
It is shown that the product of the title reaction with *tert*-butylacetylene and ethyl cyanoformate is not ethyl 3,5-di-*tert*-butyl-2-picolinate as reported in the recent literature but rather the 4,5-isomer. Varying yields of the 4,6-isomer are also obtained. The NMR spectra described for the 3,5-dimethyl analogue likewise suggest a misassignment of structure in that case. A revised mechanism is tentatively given for these reactions.

For reasons we hope to describe in a future publication, we have found ourselves in need of substantial quantities of 3,5-di-*tert*-butylpyridine. The recently described[1] facile synthesis of ethyl 3,5-di-*tert*-butyl-2-picolinate seemed to offer the best approach; it is one of a series of reports describing the multifaceted chemistry of aluminum bromide complexes of acetylenes. Thus, when *tert*-butylacetylene is treated with 1 equiv of aluminum bromide in methylene chloride at −85 °C, a 2:2 complex is produced, the ^1H and ^{13}C NMR spectra of which strongly suggest structure **1**-*t*-Bu. Complexes of this sort react with many

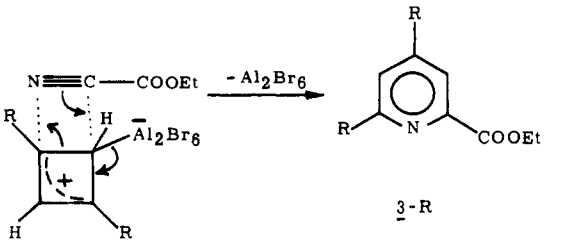


1-R

substrates to give rise to a remarkable variety of products; a summary of this chemistry was included in a recent publication.[2] In the case of activated nitriles such as ethyl cyanoformate, for example, cycloaddition to **1**-*t*-Bu occurs to give a product described as **2**-*t*-Bu. Under the same conditions, the propyne complex **1**-Me was reported to lead to the two cycloaddition products **2**-Me and **3**-Me. It was postulated that these two products were formed by the addition of the nitrile with, effectively, either the nitrogen or carbon atom displacing the aluminum:



2-R



3-R

The evidence offered for the structure of these products—obtained in analytical purity—was based on the

† SUNY.
‡ University of Groningen.

(1) Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 989.
(2) Hogeveen, H.; Kok, D. M. "Supplement C, the Chemistry of Triple-bonded Functional Groups, Part 2"; Patai, S., Rappoport, Z, Eds.; Wiley: Chichester UK, 1983.

0022-3263/84/1949-1338$01.50/0

NMR spectra of the prior complexes and of the products themselves.

We now describe results of further work in this area that differ from those reported earlier in several ways. First, we find that the formation of the reported *tert*-butylpyridine derivative is usually accompanied by that of **3**-*t*-Bu. Thus, after initial workup, the proton NMR spectrum of the crude methylene chloride solution shows two pairs of 1:1 signals in the aromatic region rather than one. The two isomers are readily separated by extracting the organic solution with dilute hydrochloric acid; the compound reported as **2**-*t*-Bu is then found in the aqueous phase and **3**-*t*-Bu remains in the organic layer. Presumably the highly hindered nitrogen atom in the latter compound is not as readily protonated; this phenomenon is well-known, for example, in 2,6-di-*tert*-butylpyridine.[3] We find that the ratio of the two products is very sensitive to the conditions, varying from 90/10 to 10/90, and we are not able to say with certainty what controls the ratio. The rate of addition of the acetylene and the length of time elapsed before the nitrile is added appeared to be important, with longer times favoring **3**-*t*-Bu; the reaction time and temperature profile of the nitrile addition may also have had effects. To prove the structure of **3**-*t*-Bu, we analyzed its ^{13}C and ^{1}H NMR spectra in the manner detailed below and found them to agree with expectations; we then hydrolyzed it by means of the trimethylsilyl iodide procedure[4] and decarboxylated the picolinic acid obtained: this gave the known[5] 2,4-di-*tert*-butylpyridine, identified via its spectral characteristics.

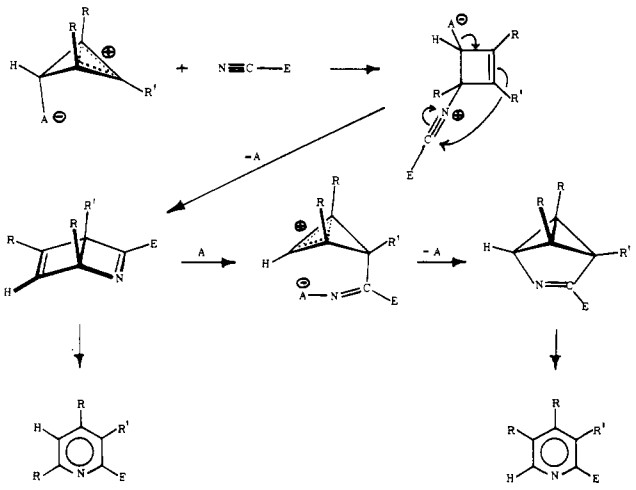
A more serious discrepancy concerns the structure reported[1] as **2**-*t*-Bu. The agreement between the observed and calculated ^{13}C spectra is now poor (see below); when the compound is hydrolyzed and the acid decarboxylated, the resulting pyridine does not have the single *tert*-butyl signal and 2:1 singlets in the aromatic region expected from 3,5-di-*tert*-butylpyridine. Rather, it reveals two high-field singlets of equal intensity (9 H each) and three signals in the aromatic region with equal intensities (1 H each). The C_{2v} structure is obviously ruled out. Detailed examination of the ^{1}H and ^{13}C NMR spectra leads us to the unambiguous assignment of 3,4-di-*tert*-butylpyridine as the structure of this product. The main supporting arguments are the facts that both α positions are unsubstituted as shown by the low-field signals, that one of the α protons is strongly coupled with another proton (J = 5.5 Hz), and, finally, that the ^{13}C NMR shifts agree closely with those calculated on the basis of an additivity scheme deriving its data from pyridine and 3- and 4-*tert*-butylpyridine.

The calculated chemical shifts are obtained as follows.[6] If δ_2, $\delta_{2(2X)}$, $\delta_{2(5Y)}$, and $\delta_{2(2X,5Y)}$ represent the ^{13}C chemical shifts of the carbon atom in the 2-position of pyridine and in the appropriately substituted pyridines, respectively, then

$$\delta_{2(2X,5Y)} = \delta_{2(2X)} + \delta_{2(5Y)} - \delta_2$$

For instance, when X and Y are both methyl, the data in the Sadtler file[7] allow one to estimate a value for the chemical shift for carbon two in 2,5-lutidine (158.3 + 146.8 − 150.6 = 154.5) that agrees closely with the observed value

Scheme I



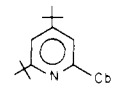
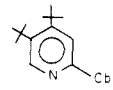
(155.2; see Table I). For all five ring carbons in that case, the agreement ranges from 0.6 to 1.0 and averages 0.8 ppm. The extension to more than two substituents is obvious. The agreement becomes less good (1–6 ppm) when two or more of the substituents are in contiguous positions. Using the Sadtler data for the ring carbons 2–6 in ethyl 2-picolinate and 4-*tert*-butylpyridine, our own data for 3-*tert*-butylpyridine, and a calculated value for **2**-*tert*-butylpyridine (from Sadtler's 4- and 2,4-di-*tert*-butylpyridine), we calculate ring carbons 2–6 in **2**-*t*-Bu to have shifts of 140.6, 144.0, 129.2 (d), 146.0, and 142.1 (d), respectively.[8] The reported shifts[1] are 157.9, 144.5, 124.2 (d), 146.8, and 150.8 (d); obviously, this is a poor fit. On the other hand, the values calculated for ethyl 3,4- and 4,5-di-*tert*-butyl-2-picolinate fit substantially better; the details may be gleaned from the table. Our assignment as the 4,5-isomer is based on the proton NMR; the aromatic region shows two sharp singlets. In **3**-*t*-Bu, the agreement between observed and calculated ^{13}C shifts is very good (0.4 ppm), presumably because of the absence of ortho disubstitution.

When the ^{13}C NMR shifts are similarly evaluated for the products of the propyne reaction, the same difficulty appears. For compound **3**-Me, the calculated shifts agree closely with those reported and, hence, this structure is correct; for the other isomer obtained, the observed shifts cn readily be reconciled with those calculated for ethyl 4,5-dimethyl-2-picolinate, but not for **2**-Me. In the $AlBr_3$-promoted cycloaddition of propyne and 2-butyne followed by treatment with ethyl cyanoformate the structure given as ethyl 3,4,5-trimethylpicolinate appears to be correct (Table I).

A mechanism that rationalizes all products is shown in Scheme I (A = Al_2Br_6, E = COOEt). The zwitterions are written in the form of homocyclopropenium ions;[9] their collapse to Dewarbenzene and benzvalene analogues has ample precedent.[10] When R′ is hydrogen, both types of pyridines appear as products; when R and R′ are both methyl, only the latter product is formed. If this proposal

(3) Brown, H. C.; Kanner, B. *J. Am. Chem. Soc.* **1966**, *88*, 986.
(4) Benkeser, R. A.; Mozdzen, E. C.; Muth, C. L. *J. Org. Chem.* **1979**, *44*, 2185.
(5) Scalzi, F. V.; Golob, N. F. *J. Org. Chem.* **1971**, *36*, 2541.
(6) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1976; p 47 ff. Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley-Interscience: New York, 1980; p 29 ff.
(7) "The Sadtler Standard Spectra"; Sadtler Research Laboratories: Philadelphia, PA, 1979.
(8) Doublets assigned on the basis of attached-proton tests, see: Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535. In the literature cited,[1] actual decoupling was used.
(9) For NMR evidence, see: Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233. For X-ray diffraction evidence, see: Krüger, C.; Roberts, P. J.; Isay, Y. H.; Koster, J. B. *J. Organomet. Chem.* **1974**, *78*, 69.
(10) Corey, E. J.; Pirkle, W. H. *Tetrahedron Lett.* **1967**, 5255. Fongers, K. S.; Hogeveen, H.; Kingma, R. F. *J. Org. Chem.* **1983**, *48*, 4275. Reeves, P.; Henery, J.; Pettit, R. *J. Am. Chem. Soc.* **1969**, *91*, 5888. Eisenharth, P.; Maas, G.; Regitz, M. *Ibid.* **1983**, *105*, 5134.

Table I. ^{13}C Chemical Shift Data in Several Pyridine Rings[a]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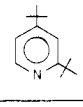
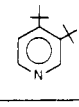
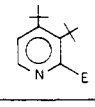
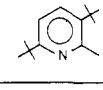
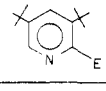
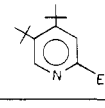
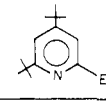
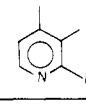
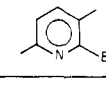
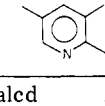
carbon[c] 2	150.6	148.4	158.3	150.1	149.5	170.0	147.0	149.6	144.9	146.1
3	124.5	125.1	123.0	133.1	124.7	121.5	145.4	120.6	118.3	125.4
4	136.4	137.2	135.9	136.4	147.2	136.5	132.4	159.5	163.9	164.2
5	124.5	127.1	120.6	123.2	124.7	119.3	122.5	120.6	120.9	143.8
6	150.6	149.9	149.1	146.8	149.5	149.5	146.4	149.6	165.2	148.6

										
source[b]	calcd	calcd	S	S	calcd	S	calcd	calcd	calcd	calcd
carbon[c] 2	157.8	157.2	155.2	157.6	149.0	147.5	146.4	156.7	153.4	155.2
3	131.6	123.2	122.7	120.1	133.3	132.3	132.5	131.8	121.9	130.8
4	135.9	146.7	136.9	136.5	147.2	137.0	147.8	146.7	146.7	136.5
5	119.3	120.8	129.8	120.1	123.4	132.3	132.5	119.5	129.4	128.4
6	145.3	148.0	149.3	157.6	145.7	147.5	146.4	144.2	147.5	146.0

								
source[b]	calcd	S	exptl	calcd	S	calcd	exptl	calcd	calcd	calcd
carbon[c] 2	166.4	169.0	169.4	165.8	167.5	146.0	150.8	142.8	143.8	143.7
3	142.4	117.6	118.2	119.5	115.2	141.5	143.5	143.4	142.1	140.8
4	132.5	159.6	160.3	132.5	135.9	155.5	157.5	128.4	156.3	133.3
5	117.3	115.4	116.1	140.2	115.2	118.6	123.3	143.4	121.2	122.1
6	145.3	148.5	148.7	145.9	167.5	145.4	146.8	142.8	144.7	165.1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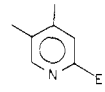
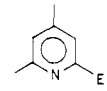
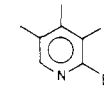
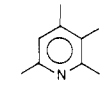
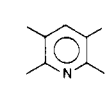
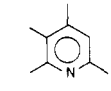
carbon[c] 2	140.6	157.9	143.2	147.4	148.0	147.7	148.5	148.8	145.3	145.2
3	144.0	144.5	119.2	124.7	118.7	119.0	141.9	138.4	132.9	144.8
4	129.2	124.2	156.3	158.4	161.1	161.1	147.2	136.9	137.8	124.5
5	146.0	146.8	144.1	144.8	118.8	119.3	122.1	121.4	134.9	134.8
6	142.1	150.8	145.3	151.3	167.2	166.5	141.9	151.4	146.8	148.8

						
source[b]	calcd	lit.[1,e]	calcd	lit.[1]	calcd	lit.[1]	calcd	calcd	calcd
carbon[c] 2	143.5	145.2	145.8	148.2	144.2	145.1	146.0	143.3	142.0
3	124.0	124.5	121.4	123.2	133.1	130.7	130.6	129.1	120.1
4	148.0	144.8	147.5	147.5	148.6	145.8	148.5	137.7	147.5
5	135.9	134.8	125.8	127.4	135.1	133.2	125.5	133.9	134.4
6	148.3	148.8	156.5	158.4	145.7	146.0	153.4	154.0	156.0

[a] Cb = COOH; E = $COOC_2H_5$. [b] S = Sadtler files (ref 7); exp = experimental (this work). The carbons were assigned on the basis of the attached-proton test,[8] proton chemical shifts, and best fit with calculated values; literature[1] data were assigned by us on the basis of proton-decoupling tests and best fits. [c] C_2 is the carbon to the right of the N atom as drawn, counting continuous and counterclockwise. [d] From 4- and 2,4-di-*tert*-butylpyridine and pyridine. [e] Our reassignment.

is correct, the structures given in ref 1 as **10a**, **10b**, **15a**, and **16b** will need revision.

Experimental Section

^1H and ^{13}C NMR spectra were recorded with a Nicolet NF-T-300, IR spectra with a Perkin-Elmer 137 (NaCl), and UV spectra with a Cary-14 spectrophotometer. The pyridine ring ^{13}C chemical shifts are omitted in the text below in favor of Table I. All NMR spectra were determined in $CDCl_3$ and all UV spectra in MeOH. GC separations were carried out with a Varian Aerograph 970 equipped with an OV-17 column operating at 140 °C. Melting and boiling points are uncorrected.

Ethyl 4,6-Di-*tert*-butyl-2-picolinate (3-*t*-Bu). CH_2Cl_2 (25 mL) precooled to −78 °C was added to 5.4 g (20 mmol) of $AlBr_3$ under a nitrogen atmosphere at −90 °C with continuous stirring. After 15 min, 1.64 g (20 mmol) of *tert*-butylacetylene[11] in 25 mL of CH_2Cl_2 (precooled to −78 °C) was added slowly (1 $^1/_2$ h). The resulting red-brown solution was stirred for an additional $^1/_2$ h at −90 °C. Then 2.5 mL (25 mmol) of ethyl cyanoformate in 3 mL of CH_2Cl_2 (precooled to −78 °C) was added dropwise (15 min) and the resulting solution stirred at −90 °C for 2 h. The flask was allowed to warm slowly to 0 °C and the reaction mixture was quenched with 200 mL of 1 M NaOH, and the aqueous layer was isolated and extracted with ether (3 × 100 mL). The organic layers

(11) (a) Brandsma, L.; Verkruysse, H. D. "Syntheses of Acetylenes, Allenes, and Cumulenes"; Elsevier: New York, 1981; p 119. (b) Collier, W. L.; Macomber, R. S. *J. Org. Chem.* **1973**, *38*, 1367.

were combined, dried over anhydrous $MgSO_4$, and filtered; the solvent was evaporated to give 212 mg (8.1%) of a pale yellow oil, which was further purified by GC. ^1H NMR δ 1.34 (s, 9 H), 1.42 (s, 9 H), 1.48 (t, J = 8 Hz, 3 H), 4.43 (q, J = 8 Hz, 2 H), 7.48 (d, J = 1.5 Hz, 1 H), 7.89 (d, J = 1.5 Hz, 1 H); ^{13}C NMR δ 14.6, 30.5, 30.9, 35.2, 38.1, 61.5, 169.7; IR (neat) 1710 cm^{-1}; UV λ_{max} 271 nm (ϵ 3540), 228 nm (ϵ 8600); MS, m/z 263 (M^+). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32. Found: C, 72.91; H, 9.36; N, 5.53.

Ethyl 4,5-Di-*tert*-butyl-2-picolinate. The previous experiment is repeated with the following changes. The addition of the *tert*-butylacetylene is completed in $^1/_2$ h, the subsequent stirring in 15 min, the addition of ethyl cyanoformate in 10 min, and the final stirring in 15 min. This yields 627 mg (23.8%) of crude product that was further purified by dissolution in 150 mL hexanes and extraction with 1 N HCl (3 × 100 mL). The combined acidic water layers were then made alkaline with concentrated NaOH and extracted with CH_2Cl_2 (2 × 100 mL), the combined orgnaic layers were dried over $MgSO_4$ and filtered, and the solvent was removed. The resulting pale yellow oil was crystallized from pentane to afford a cream-colored solid, mp 61–62 °C lit.[1] mp 62.5–63.5 °C: ^1H NMR δ 1.45 (t, J = 7.5 Hz, 3 H), 1.57 (s, 9 H), 1.60 (s, 9 H), 4.47 (q, J = 7.5 Hz, 2 H), 8.29 (s, 1 H), 8.90 (s, 1 H); ^{13}C NMR δ 14.4, 33.8, 34.2, 36.9, 37.9, 61.5, 165.8; IR ($CHCl_3$) 1710 cm^{-1}; UV λ_{max} 265 nm (ϵ 6890), 233 nm (ϵ 14640); MS, m/z 263 (M^+).

4,5-Di-*tert*-butyl-2-picolinic Acid. To a mixture of 52.6 mg (0.2 mmol) of the ethyl ester and 5.08 mg (0.02 mmol) of I_2 in a 10-mL round-bottomed flask was added 0.4 g (2 mmol) of trimethylsilyl iodide under a nitrogen atmosphere. The solution was stirred and refluxed in an oil bath at 125 °C for 24 h, allowed to cool, evaporated at low pressure to small volume, quenched with 10 mL of water followed by 10 mL of a saturated $Na_2S_2O_3$ solution, and extracted with $CHCl_3$ (3 × 10 mL). The organic layers are combined and dried over anhydrous $MgSO_4$, filtered, and evaporated to give a cream-colored solid. Recrystallization from $CHCl_3$ gave 34.3 mg (73%) of white needles: mp 209 °C; ^1H NMR δ 1.59 (s, 9 H), 1.63 (s, 9 H), 8.52 (s, 1 H), 9.26 (s, 1 H), 15.10 (s, 1 H); ^{13}C NMR δ 33.6, 34.0, 37.4, 38.7, 164.2; IR ($CHCl_3$) 1750, 2400, 3650 cm^{-1}; UV λ_{max} 274 nm (ϵ 7960), 228 nm (ϵ 13760); MS, m/z 235 (M^+). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.49; H, 8.94; N, 5.96. Found: C, 71.30; H, 8.93; N, 5.82.

4,6-Di-*tert*-butyl-2-picolinic acid was obtained similarly from the ethyl ester in 42% yield as a light brown solid. Recrystllization from pentane gives a white solid; mp 138 °C; ^1H NMR δ 1.36 (s, 9 H), 1.41 (s, 9 H), 7.61 (d, J = 2.5 Hz, 1 H), 8.08 (d, J = 2.5 Hz, 1 H); ^{13}C NMR δ 30.5, 31.0, 35.8, 37.8, 168.7; IR ($CHCl_3$) 1750, 2400, 3650 cm^{-1}; UV λ_{max} 269 nm (ϵ 2350), 227 nm (ϵ 1990); MS, m/z 235 (M^+). Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.49; H, 8.94; N, 5.96. Found: C, 71.3; H, 8.90; N, 5.80.

3,4-Di-*tert*-butylpyridine. A sample of 100 mg (0.42 mmol) of 4,5-di-*tert*-butyl-2-picolinic acid is placed in a small glass tube (4 × $^1/_4$ in.), which is closed with a serum cap and purged with nitrogen. While the tube remains connected to the bubbler, it is lowered into an oil bath at 210–220 °C. After the solid melts, bubbling is observed to become more vigorous. After the reaction a viscous yellow liquid remains; it is purified by GC to yield a clear colorless liquid: ^1H NMR δ 1.52 (s, 9 H), 1.56 (s, 9 H), 7.39 (d, J = 5.5 Hz, 1 H), 8.29 (d, J = 5.5 Hz, 1 H), 8.75 (s, 1 H); ^{13}C NMR δ 33.9, 34.4, 36.6, 37.7; UV λ_{max} 266 nm (ϵ 2620), 225 nm (ϵ 1265); MS, m/z 191 (M^+). Anal. Calcd for $C_{13}H_{21}N$: C, 81.67; H, 11.0; N, 7.33. Found: C, 80.97; H, 11.17; N, 7.17.

2,4-Di-*tert*-butylpyridine. 4,6-Di-*tert*-butyl-2-picolinic acid is placed in a micro distillation apparatus and heated in an oil bath at 220 °C. It melts at 138 °C but the evolution of gas does not commence until about 200 °C. As the acid decarboxylates, the product distils over as a light yellow oil, bp 210 °C: ^1H NMR δ 1.30 (s, 9 H), 1.37 (s, 9 H), 7.07 (dd, J = 2 Hz, 5 Hz, 1 H), 7.31 (dd, J = 0.7 Hz, 2 Hz 1 H), 8.45 (dd, J = 0.7 Hz, 5 H, 1 H); ^{13}C NMR[7] δ 30.8, 31.1, 35.2, 37.9; UV λ_{max} 266 nm (ϵ 2260), 259 nm (ϵ 3922); MS, m/z 191 (M^+).

3-*tert*-Butylpyridine. This was prepared on a 10-g scale from 3-picoline as described by Howie and Brown:[12] ^1H NMR δ 1.40 (s, 9 H), 7.20 (ddd, $J_{2,5}$ = 0.86 Hz, $J_{5,6}$ = 4.7 Hz, $J_{4,5}$ = 8.2 Hz, 1 H), 7.65 (ddd, $J_{4,6}$ = 1.7 Hz, $J_{2,4}$ = 2.6 Hz, 1 H), 8.4 (dd, 1 H), 8.65 (dd, 1 H); ^{1C} NMR δ 30.6, 33.2.

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Registry No. *tert*-Butylacetylene, 917-92-0; ethyl cyanoformate, 623-49-4; aluminum bromide, 7727-15-3; ethyl 4,5-di-*tert*-butyl-2-picolinate, 89032-16-6; ethyl 4,6-di-*tert*-butyl-2-picolinate, 89032-17-7; 4,5-di-*tert*-butyl-2-picolinic acid, 89032-18-8; 4,6-di-*tert*-butyl-2-picolinic acid, 89032-19-9; 3,4-di-*tert*-butylpyridine, 89032-20-2; 2,4-di-*tert*-butylpyridine, 29939-31-9; 3-*tert*-butylpyridine, 38031-78-6.

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Palladium-Catalyzed Decarboxylation–Carbonylation of Allylic Carbonates To Form β,γ-Unsaturated Esters

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Allyl alkyl carbonates undergo a smooth decarboxylation–carbonylation reaction to afford β,γ-unsaturated esters at 50 °C under atmospheric or low pressure of carbon monoxide and neutral conditions in the presence of palladium–phosphine complexes as catalysts. The reaction offers a very good method for the preparation of β,γ-unsaturated esters from allylic alcohols.

Various allylic compounds such as allylic halides, esters, ethers, and amines undergo several types of transformations in the presence of palladium–phosphine complexes as catalysts, and extensive studies have been carried out on these reactions.[1] However, one reaction of allylic compounds which receives much less attention is the carbonylation. We have shown that π-allylpalladium chloride can be converted to 3-butenoate under carbon monoxide pressure in alcohol.[2] Recently, Milstein carried out the carbonylation of π-allylpalladium complexes under mild conditions (25 °C, 50 psi) with added sodium car-

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