Anal. Calcd for $C_{23}H_{32}N_8O_9 \cdot 1.25H_2O$: C, 46.69; H, 5.96; N, 18.94. Found: C, 46.32; H, 5.93; N, 18.70.

Evaporation of the ammonia eluate gave **2b** (9 mg, 18%) as identified by TLC (S_1 and S_2). A similar workup of the aqueous portion afforded **3** (16 mg, 32%).

Acknowledgment. The authors are indebted to Mrs. E. Stanley from the Wayne State University Computer Services Center for computer work. The NMR spectra were measured by Dr. D. P. Lin and Messrs. S. Grunfeld and K. L. Hsu.

Registry No. 1, 65-46-3; **2a**, 73611-47-9; **2b**, 73611-48-0; **2c**, 22342-50-3; **3**, 5399-87-1; **4a**, 73611-49-1; **4b**, 73611-50-4; 1,2-diaminoethane, 107-15-3; 1,4-diaminobutane, 110-60-1; ethylamine, 75-04-7.

Notes

Synthesis of Spiro-Activated Cyclopropanes from Alkenes via the Irradiation of Isopropylidene Diazomalonate. A Reinvestigation

Robert V. Stevens,* Gregory S. Bisacchi, Larry Goldsmith,
and C. E. Strouse

Department of Chemistry, University of California,
Los Angeles, California 90024

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"Spiro-activated" cyclopropanes 1 have been demonstrated to be valuable intermediates in organic synthesis.[1] Recently, we reported[2] a simple method for the preparation of these intermediates by the direct irradiation (253.7 nm) of isopropylidene diazomalonate (**2**) in the presence of an olefin. A number of olefins were investigated, including 1,3,3-trimethylcyclohexene which was reported to afford adduct **3**. However, recent attempts to employ **3** as an intermediate in a projected synthesis led us to doubt the structure (**3**) assigned originally. Accordingly, we undertook an X-ray crystallographic analysis of this substance. Crystallographic data were obtained at 115 K with a Syntex P1 diffractometer equipped with a locally constructed low-temperature device.[3] Experimental and data-handling techniques were analogous to those described previously.[4] Experimental parameters are summarized in footnote 5. Direct-methods (MULTAN), difference-Fourier, and least-squares refinement techniques were used in the solution of the structure. In the final refinement, positions and anisotropic thermal parameters of all nonhydrogen atoms were refined along with the positions of the hydrogen atoms. Isotropic temperature factors of the hydrogen atoms were fixed at 2.0 Å^2. As Figure 1 reveals, this compound was not cyclopropane **3** as reported previously, but rather the cyclobutanone **4a**.

This result can be rationalized in terms of a Wolff rearrangement of the initially formed carbene (**5**) to afford ketene **6**[7] which undergoes a remarkably regio- and stereospecific cycloaddition[8] to the olefin to afford cyclo-

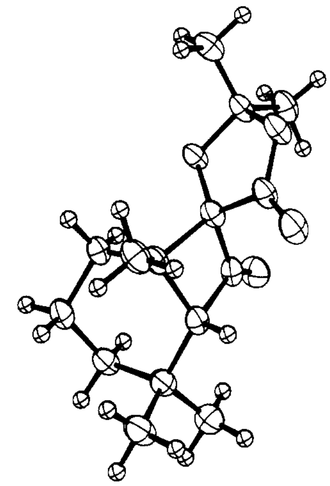
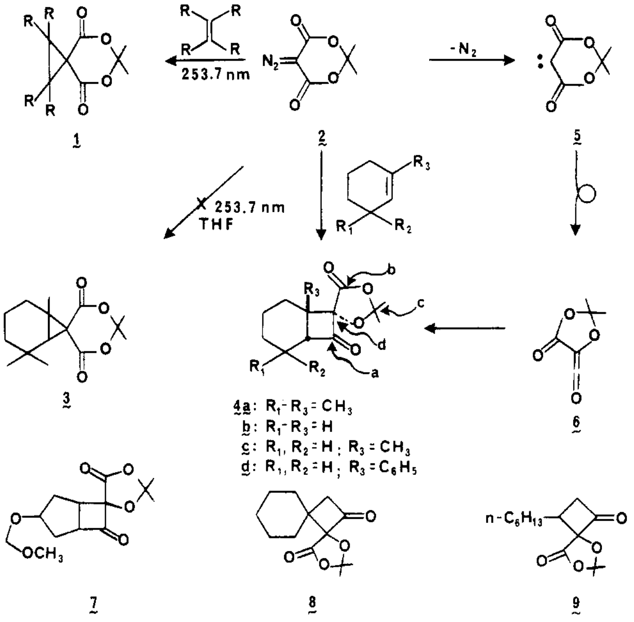


Figure 1.

Scheme I



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[1] S. Danishefsky, *Acc. Chem. Res.*, **12**, 66 (1979), and references cited therein.

[2] (a) T. Livinghouse and R. V. Stevens, *J. Am. Chem. Soc.*, **100**, 6479 (1978); (b) R. V. Stevens, *Pure Appl. Chem.*, **51**, 1317 (1979).

[3] C. E. Strouse, *Rev. Sci. Instrum.*, **47**, 891 (1976).

[4] J. Strouse, S. W. Layten, and C. E. Strouse, *J. Am. Chem. Soc.*, **99**, 562 (1977).

[5] Crystal data: space group $P2_1/C$; $Z = 4$; lattice parameters (115 K), $a = 10.966$ (3) Å, $b = 8.128$ (2) Å, $c = 17.805$ (3) Å, $\beta = 113.02$ (2)°; radiation, Cu K crystal monochromatized (1.5418 Å); crystal dimensions, 0.17 × 0.20 × 0.20 mm; absorption coefficient, 7.16 cm^{-1}; $T_{\min} = 0.80$, $T_{\max} = 0.85$; scan range, 1.0 below Kα_1 to 1.0 above Kα_2; scan rate, 6.0°/min; scan mode, θ–2θ; $2\theta_{\max} = 110°$; background time = scan time; observed reflections [I greater than 3.0(σI)], 1728, $R = 0.042$, $R_w = 0.059$, error in observation of unit weight of 2.24.

[6] Such a rearrangement in methanol-benzene but at unspecified wavelength has been reported previously: S. L. Kammula, H. L. Tracer, P. B. Shevlin, and M. Jones, Jr., *J. Org. Chem.*, **42**, 2931 (1977).

[7] Ketene **6** has been identified spectroscopically by photolysis of **2** in an argon matrix: private communication from Professor O. L. Chapman and R. Hayes, Department of Chemistry, University of California, Los Angeles.

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butanone **4a**. With this structure firmly established, examination of the data (^{1}H NMR and IR) included in our initial paper leads us to conclude that none of the adducts reported were cyclopropanes and that each should be reformulated as a cyclobutanone. In particular, the infrared spectra show two carbonyl absorptions—one in the range 1766–1782 cm^{-1}, typical of cyclobutanones, and a second in the range 1789–1801 cm^{-1}, characteristic of lactones of this type.[9] Further corroboration is provided from the ^{13}C NMR spectra of adducts **4a–d** and **7–9**. Each of these substances shows singlet resonances in the ranges 198.9–205.3 ppm (carbon a), 166.2–169.3 (carbon b), 110.5–112.0 (carbon c), and 92.3–96.5 (carbon d). In view of these findings, our additional claim[10,2b] to have effected homoconjugate openings of these "spiro-activated cyclopropanes" with various Grignard reagents must also be disregarded.

Acknowledgment. The financial support of the National Science Foundation (Grant No. NSF CHE76-84340 and NSF CHE76-05926, Instrument Grant for the Brucker NMR 200) and the National Institutes of Health (Grant No. CA25675) is gratefully acknowledged.

Registry No. 2, 7270-63-5; **4a**, 73466-63-4; **4b**, 73454-16-7; **4c**, 73466-64-5; **4d**, 73454-17-8; **6**, 73454-18-9; **7**, 73466-65-6; **8**, 73454-19-0; **9**, 73454-20-3; 1,3,3-trimethylcyclohexene, 503-47-9; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1-phenylcyclohexene, 771-98-2; 2-(2,2-dimethyl-1,3-dioxolan-4-on-5-yl)-2,6,6-trimethylbenzoic acid, 73466-66-7.

Supplementary Material Available: Complete ^{13}C NMR data for **4a–d** and **7–9**; tables of final structural parameters and intramolecular distances and angles (6 pages). Ordering information is given on any current masthead page.

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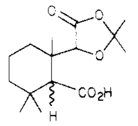
[8] We have found that in the case of 1,3,3-trimethylcyclohexene the reaction is solvent dependent. Thus, photolysis in THF produces only cyclobutanone **4a**. However, in methylene chloride, in addition to **4a**, a second extremely unstable adduct is formed which reacts with moisture in the air to produce a carboxylic acid. The spectral data (^{1}H and ^{13}C NMR, IR, and mass spectra) are consistent with those of the following structure:



[9] Infrared data for lactones of this type have been recorded by M. Farines and J. Soulier, *Bull. Soc. Chim. Fr.*, 332 (1970).

[10] T. Livinghouse and R. V. Stevens, *J. Chem. Soc., Chem. Commun.*, 754 (1978).

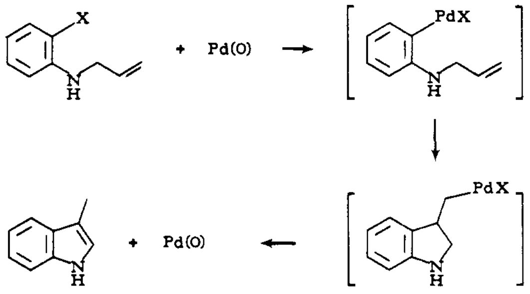
Conversion of 2-Halo-*N*-allylanilines to Indoles via Palladium(0) Oxidative Addition–Insertion Reactions

Roy Odle, Burke Blevins, Matt Ratcliff, and
Louis S. Hegedus*

Department of Chemistry, Colorado State University,
Fort Collins, Colorado 80523

Received January 18, 1980

As part of an overall program directed toward the synthesis of the mitocenes, we have considered several organometallic approaches to the indole ring systems.[1,2] A potentially attractive approach involves an intramolecular "Heck" arylation[3] of 2-halo-*N*-allylanilines (eq. 1). This procedure works rather well for systems in which the side-chain olefin is conjugated to a carbonyl group. Thus 2-halo-*N*-acryloyl- or -cinnamoylanilines are converted to oxindoles in fair yield, using both Pd(0)[4–6] and Ni(0)[7] catalysts. Similarly, 2-halo-*N*-allylanilines having ester groups γ to the nitrogen cyclize to 3-carbonyl-substituted indoles and/or quinoline in modest yield under related reaction conditions.[6,8,9] However, the only reported cyclization of this type of simple unactivated 2-halo-*N*-allylanilines involve Ni(0) catalysts and goes in rather low (20–45%) yield.[10] Since our further synthetic work required the cyclization of unactivated *N*-allylanilines, we developed closures for a number of simple systems. The results are summarized in Table I.



(1)

Typical literature procedures for "Heck arylation"[3–10] involve heating substrate, an amine, and, with bromides, a phosphine and 3% palladium acetate in acetonitrile in a sealed tube for several days at 110 °C. We have found that considerably better yields are obtained by addition of the catalyst in three successive 1% portions, one each day of reaction. Apparently the catalyst is deactivated during the reaction and periodic provision of fresh catalyst permits a higher overall yield, using the same total amount of catalyst. As is typical, the bromo aromatics are less reactive than the iodo aromatics and require the addition of 2 equiv of tris(2-tolyl)phosphine[3] per Pd to produce acceptable yields.[11]

Two substrates fail to cyclize. The *N*-cyclohexenylaniline is recovered unchanged from the reaction medium, thus prohibiting the synthesis of carbazoles by this method. The reason for this lack of reactivity is not apparent. Similarly the *N*-(2-methallyl)aniline also fails to cyclize. In this case, closure to a five-membered ring would produce a σ-alkylpalladium complex lacking β hydrogens and thus lacking the ability to β-hydride eliminate and regenerate the catalyst. However, closure to form a six-membered ring would permit β elimination. This does not occur, since the substrate is recovered unchanged from the reaction mixture. That six-membered ring formation *can* occur is shown by the closure of 2-bromo-*N*-(2-carbethoxyallyl)-

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[1] L. S. Hegedus, G. F. Allen, J. J. Bozell, and E. L. Waterman, *J. Am. Chem. Soc.*, **100**, 5800 (1978).

[2] L. S. Hegedus, G. F. Allen, and D. J. Olsen, *J. Am. Chem. Soc.*, in press.

[3] For a current review of this process, see R. F. Heck, *Acc. Chem. Res.*, **12**, 146 (1978).

[4] M. A. Terpko and R. F. Heck, *J. Am. Chem. Soc.*, **101**, 5281 (1979).

[5] M. Mori and Y. Ban, *Heterocycles*, **9**, 391 (1979).

[6] M. Mori and Y. Ban, *Tetrahedron Lett.*, 1133 (1979).

[7] M. Mori and Y. Ban, *Tetrahedron Lett.*, 1807 (1976).

[8] N. Cortese, C. B. Ziegler, Jr., B. J. Hrnjez, and R. F. Heck, *J. Org. Chem.*, **43**, 2952 (1978).

[9] M. Mori, K. Chiba, and Y. Ban, *Tetrahedron Lett.*, 1037 (1977).

[10] M. Mori and Y. Ban, *Tetrahedron Lett.*, 1803 (1976).

[11] It has been noted by J. T. Arrigo and A. K. Sparks (Universal Oil Products Company), U.S. Patent 3 707 481, 1972, that *N*-methyl-*N*-vinylaniline and *N*-methyl-*N*-allylaniline will cyclize in the presence of palladium acetylacetonate–Cu(OAc)$_2$ or palladium acetate–Cu(OAc)$_2$ to give *N*-methylindole and *N*-methyl-1,2-dihydroquinoline, respectively. No yields are reported.

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