the bath was removed and allowed to warm up to room temperature (5 h). The reaction mixture was poured into ice water and extracted with ether. The ether phase was washed with aqueous bicarbonate and dried over anhydrous sodium sulfate. The solvent was removed, and the mixture of products **10** and **11** was dissolved in 60 mL of $Me_2SO$. To this stirred mixture was introduced DBU (657 μL, 4.4 mmol) and heated at 80 °C for 10 h. The reaction mixture was poured into water and extracted with hexane. The organic phase was dried and concentrated to obtain a mixture of **12** and **13** (820 mg, 76%). These products were separated by preparative HPLC (Du Pont Zorbax ODS Column (2.12 × 25 cm), $CH_3CN$–$H_2O$ (5:1), 20 mL/min). The first fraction collected was pure olefin **12** ($k'$ = 3.6): $^1H$ NMR δ 6.67 (d, 1 H, vinyl proton, $J_{H,F}$ = 20.0 Hz), 7.06 (m, 2 H), 7.14 (m, 3 H), 7.51 (m, 3 H), 7.78 (m, 2 H), 7.94 (m, 1 H); MS (EI) $m/z$ calcd for $C_{18}H_{12}F_2$ 266.0907, found 266.0909; UV $\lambda_{max}$ at 222 nm ($CH_3CN$). The second fraction collected was the olefin **13** ($k'$ = 4.4): $^1H$ NMR δ 6.55 (d, 1 H, vinyl proton, $J_{H,F}$ = 20.0 Hz), 7.35 (m, 3 H), 7.45 (m, 4 H), 7.59 (m, 2 H), 7.73 (m, 2 H); MS (EI) $m/z$ calcd for $C_{18}H_{12}F_2$ 266.0907, found 266.0900; UV $\lambda_{max}$ at 222 nm ($CH_3CN$).

**6,7-Difluorobenzo[*c*]phenanthrene (14).** A solution of **12** (63 mg, 0.23 mmol) in 400 mL of cyclohexane containing a catalytic amount of iodine was irradiated in an immersion apparatus with a 450-W Hanovia medium-pressure mercury arc lamp contained in a water-cooled quartz probe. The solution was continuously purged with air during the irradiation, and the progress of the photocyclization reaction was monitored by HPLC. After 1.5 h, the solvent was evaporated and the crude product was chromatographed on basic Alumina (hexane) to obtain pure 6,7-difluorobenzo[*c*]pheanthrene (**14**) (22 mg, 37%): mp 131–132 °C; $^1H$ NMR δ 7.57 (dd, 2 H, H-5 and H-8, $J_{H,F}$ = 6.5 and 6.0 Hz), 7.64 (m, 4 H), 7.94 (dd, 2 H, H-4 and H-9, $J_{4,3} = J_{9,10}$ = 6.5 Hz and $J_{4,2} = J_{9,11}$ = 2.5 Hz), 8.99 (m, 2 H, H-1 and H-12); $^{19}F$ NMR δ 42.31 (dd, $J_{H,F}$ = 6.5 and 6.0 Hz); MS (EI) $m/z$ calcd for $C_{18}H_{10}F_2$ 264.0750, found 264.0754; UV ($CH_3CN$) $\lambda_{max}$ (ε, $M^{-1}$ $cm^{-1}$), 278 (41 800), 284 nm (41 800).

**5,7-Difluorobenzo[*c*]phenanthrene (15).** Photolysis of **13** (117 mg, 0.44 mmol) in 400 mL of cyclohexane with a catalytic amount of iodine for 1.5 h with the same apparatus as described above gave the photocyclized product 5,7-difluorobenzo[*c*]pheanthrene (**15**) (35 mg, 26%) following chromatography on basic Alumina (hexane): mp 112–114 °C; $^1H$ NMR δ 7.57 (d, 1 H, H-8, $J_{H,F}$ = 10.5 Hz), 7.63 (m, 2 H), 7.76 (m, 2 H), 7.80 (d, 1 H, H-6, $J_{H,F}$ = 11.0 Hz), 7.96 (dd, 1 H, H-9, $J_{9,10}$ = 7.0 Hz and $J_{9,11}$ = 2.5 Hz), 8.35 (dd, 1 H, H-4, $J_{4,3}$ = 7.0 Hz and $J_{4,2}$ = 2.5 Hz), 9.02 (d, 1 H, H-1 or H-12, $J$ = 7.5 Hz), 9.14 (d, 1 H, H-12 or H-1, $J$ = 8.0 Hz); $^{19}F$ NMR δ 37.1 (d, $J_{H,F}$ = 10.5 Hz), 39.14 (d, $J_{H,F}$ = 11.0 Hz); MS (EI) $m/z$ calcd for $C_{18}H_{10}F_2$ 264.0750, found 264.0738; UV ($CH_3CN$) $\lambda_{max}$ (ε $M^{-1}$ $cm^{-1}$), 276 (44 800), 282 nm (47 400).

**α-Bromo-β-fluoro-β-naphth-2-ylstyrene (17).** To a dry ice/acetone (−78 °C) cooled mixture of NBA (35 mg, 0.25 mmol), 2 mL of pyridinium poly(hydrogen fluoride) (70%), and 5 mL of ether in a polyolefin bottle was added the β-naphthylstyrene **16** (49 mg, 0.21 mmol) in 10 mL of ether. The reaction mixture was stirred for 5 h at this temperature and for an additional 5 h at room temperature, and then poured into water and extracted with ether. The organic phase was washed with aqueous bicarbonate, dried over $Na_2SO_4$, and concentrated to obtain **17** (67 mg, 95%). Recrystallization from $CHCl_3$/hexane gave pure **17**: mp 120–121 °C; $^1H$ NMR δ 5.23 (dd, 1 H, CHBr, $J_{H,F}$ = 15.0 Hz and $J_{\alpha H,\beta H}$ = 6.5 Hz), 6.00 (dd, 1 H, CHF, $J_{H,F}$ = 46.0 Hz and $J_{\beta H,\alpha H}$ = 6.5 Hz), 7.33 (m, 4 H), 7.41 (m, 2 H), 7.5 (m, 2 H), 7.82 (m, 4 H); MS (EI) $m/z$ calcd for $C_{18}H_{14}BrF$ 328.0263, found 328.0231; UV $\lambda_{max}$ at 224 nm ($CH_3CN$).

**β-Fluoro-β-naphth-2-ylstyrene (18).** A mixture **17** (198 mg, 0.6 mmol) and DBU (0.1 mL, 0.66 mmol) in 20 mL of $Me_2SO$ was heated at 80 °C for 8 h. The reaction mixture was poured into water and extracted with hexane. The organic phase was dried over anhydrous $Na_2SO_4$ and concentrated. The crude product was purified by HPLC (Du Pont Zorbax Silica Column (2.12 × 25 cm), 10% $CH_2Cl_2$/hexane, 20 mL/min) and recovered as a mixture of cis and trans isomers of **18** (110 mg, 74%). A partial separation of the two isomers was achieved on a small scale: cis isomer **18**, $^1H$ NMR δ 6.54 (d, 1 H, vinyl proton, $J_{H,F}$ = 22.0 Hz), 7.45 (m, 5 H), 7.75 (m, 6 H), 7.98 (s, 1 H); trans isomer **18**, $^1H$ NMR δ 6.46 (d, 1 H, vinyl proton, $J_{H,F}$ = 40.0 Hz), 7.40 (m, 2 H), 7.51 (m, 2 H), 7.71 (m, 3 H), 7.86 (m, 4 H), 8.13 (s, 1 H); MS (EI) $m/z$ calcd for $C_{18}H_{13}F$ 248.1001, found 248.0993; UV (both isomers) $\lambda_{max}$ at 226 nm ($CH_3CN$).

**6-Fluorobenzo[*c*]phenanthrene (19).** A solution of **18** (30 mg, 0.12 mmol) in 300 mL of cyclohexane with a catalytic amount of iodine was irradiated as described earlier for 1.5 h. The solvent was evaporated, and the crude product was chromatographed on basic Alumina (hexane) to obtain pure **19** (15 mg, 50%): mp 71–72 °C (lit.[6] mp 72–73 °C); $^1H$ NMR δ 7.54 (d, 1 H, H-5, $J_{H,F}$ = 11.0 Hz), 7.7 (m, 4 H), 7.95 (m, 1 H, H-4 or H-9), 7.99 (d, 1 H, H-8, $J_{8,7}$ = 9.0 Hz), 8.03 (d, 1 H, H-9 or H-4, $J$ = 7.3 Hz), 8.16 (d, 1 H, H-7, $J_{7,8}$ = 9.0 Hz), 9.12 (2 d, 2 H, H-1 and H-12, $J$ = 10.0 and 9.0 Hz); UV $\lambda_{max}$ at 274 nm ($CH_3CN$).

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# Catalytic Cyclopropanation of Alkenes with Ethyl Nitrodiazoacetate. A Facile Synthesis of Ethyl 1-Nitrocyclopropanecarboxylates

P. E. O'Bannon and William P. Dailey*

*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323*

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Ethyl 1-nitrocyclopropanecarboxylates are formed in the reaction between alkenes and ethyl nitrodiazoacetate using a catalytic amount of rhodium(II) acetate. Ethyl oxo[hydroxy(alkyl-2-propenyl)amino]acetates are obtained as side products. These result from an ene reaction between the alkene and an intermediate acyl nitroso compound. Relative reactivities and stereoselectivities for catalytic rhodium(II) acetate reactions of ethyl nitrodiazoacetate with 12 alkenes to yield cyclopropanes and ene products are reported. Electron-rich, sterically undemanding alkenes are the most reactive and give the best yields of cyclopropanes. Less reactive, crowded alkenes give poor yields of cyclopropanes and enhanced yields of ene products. A comparison with the relevant data for ethyl diazoacetate reveals that the reaction with ethyl nitrodiazoacetate is more sensitive to the electronic and steric nature of the reactant alkene. Doyle's model for catalytic cyclopropanation with rhodium(II) acetate is invoked to explain these data.

There has recently been considerable effort directed at the synthesis and study of strained ring nitro compounds as high-energy density materials.[1] Nitrocyclopropanes are the simplest members of this class of compounds. Al-

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**Table I. Relative Reactivities, Product Yields, and Stereoselectivities for $Rh_2(OAc)_4$-Catalyzed Reactions of Ethyl Nitrodiazoacetate and Ethyl Diazoacetate with Several Alkenes**

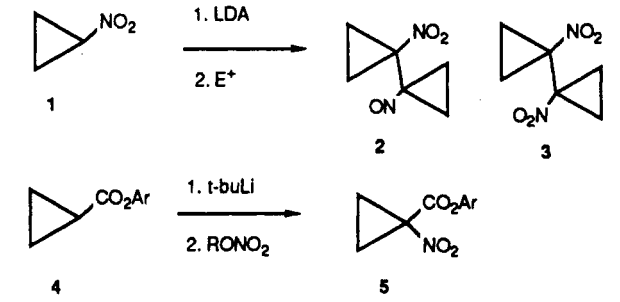
| | | ethyl nitrodiazoacetate | | | | ethyl diazoacetate[a] | | |
|---|---|---|---|---|---|---|---|---|
| entry | olefin | % cyc[b] | cis/trans[c] | % ene[b] | rel rate[d] | % cyc | cis/trans | rel rate[d] |
| 1 | ethyl vinyl ether | 0[e] | | – | | 88 | 0.59 | 8.3 |
| 2 | styrene | 75 | 8.0 | – | 17.0 | 93 | 0.63 | 3.5 |
| 3 | 2-methylpropene | 75 | *f* | *i* | *h* | | | |
| 4 | vinyl acetate | 55 | 3.0[g] | – | 3.5 | 59 | 0.63 | 1.1 |
| 5 | *cis*-2-butene | 65 | 4.0 | 13 | *h* | | | |
| 6 | 1-hexene | 35 | 1.1 | *i* | 1.0 | 95 | 0.67 | 1.0 |
| 7 | cyclohexene | 35 | 6.0 | 25 | 0.43 | 90 | 0.26 | 2.5 |
| 8 | 2-methyl-2-butene | 20 | 2.5 | 44 | 0.17 | 97 | 0.67 | 1.5 |
| 9 | *trans*-β-methylstyrene | 20 | 2.0[g] | *i* | 0.17 | | | |
| 10 | 3-methyl-1-butene | 22 | 1.3 | *i* | 0.37 | 58 | 0.50 | 0.86 |
| 11 | 3,3-dimethyl-1-butene | 3 | 0.8 | – | 0.063 | 87 | 0.24 | 0.67 |
| 12 | *trans*-2-butene | 0 | | 86 | | | | |
| 13 | 2,3-dimethyl-2-butene | 0 | | 81 | | | | |

[a] Taken from ref 12. [b] Reproducible, isolated yields. [c] Ratios were determined by $^1H$ NMR, GC, and chemical methods. Substituents are defined as cis or trans relative to the carboethoxy group. [d] Relative to 1-hexene. [e] Products were unstable. [f] Only one isomer possible. [g] Cis isomer could not be separated from trans isomer via saponification. [h] Relative rate not measured. [i] While ene products are possible, none could be isolated in these cases.

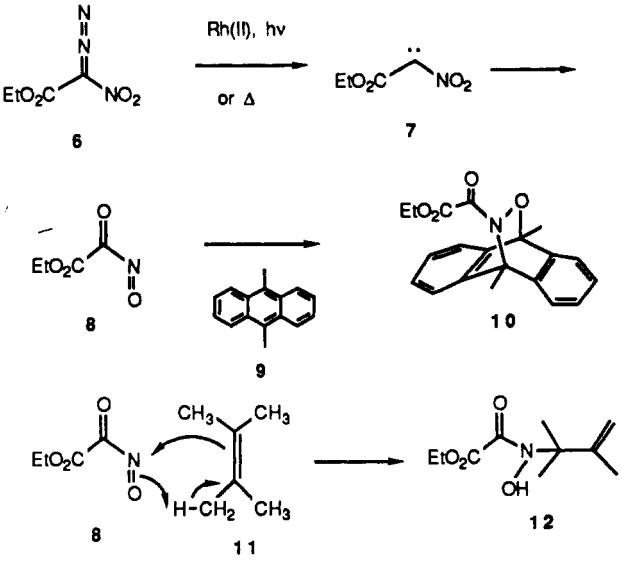
though there are several preparative methods for nitrocyclopropanes,[2] an obvious choice, the addition of nitrocarbene to an alkene, has only recently be described by us.[3] In fact, despite the wealth of information on carbenes,[4] only a handful of publications pertaining to nitrocarbenes exist.[5] The most significant of these are from Schöllkopf and co-workers. They developed syntheses for nitrodiazomethane and nitrodiazo esters.[5a,c] Although diazo compounds are ideal precursors to carbenes, photolysis or thermolysis of ethyl nitrodiazoacetate or nitrodiazomethane in the presence of 2,3-dimethyl-2-butene afforded no cyclopropanes and no other products that would indicate formation of the nitrocarbene.[5b] Despite this seemingly bleak outlook for nitrocarbene chemistry, we found that rhodium(II) acetate[6] will transfer nitrocarbene from nitrodiazomethane to electron-rich alkenes.[3]

While this method provides an entry to nitrocyclopropanes that are otherwise inaccessible, the reaction has several drawbacks. The yields of cyclopropanes range from poor to moderate, and, importantly, there is an ever present danger of explosion when working with nitrodiazomethane and it's precursor, nitrodiazoacetic acid.[7] On the other hand, ethyl nitrodiazoacetate may be prepared in decagram quantities by nitration of ethyl diazoacetate and stored for months at 5 °C without danger of explosion or decomposition.

**Scheme I**




**Scheme II**




We sought to extend this cyclopropanation reaction to ethyl nitrodiazoacetate (6). This would provide access to 1-nitrocyclopropane carboxylates. Subsequent saponification and decarboxylation would provide a roundabout route to nitrocyclopropanes. Moreover, 1-substituted nitrocyclopropanes are not easily prepared.[8] Seebach and co-workers have shown that deprotonation of nitrocyclopropane (1) with LDA and subsequent addition of an

(1) (a) Wade, P. A.; Dailey, W. P.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 5452. (b) Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. (c) Archibald, T. G.; Baum, K. *J. Org. Chem.* **1988**, *53*, 4645. (d) Waycole, L. M.; Shen, C.; Paquette, L. A. *J. Org. Chem.* **1988**, *53*, 4969. (e) Review: Marchand, A. P. *Tetrahedron* **1988**, *44*, 4645.

(2) (a) Asunskis, J.; Shechter, H. *J. Org. Chem.* **1968**, *33*, 1164. (b) Parham, W. E.; Braxton, H. G.; Serres, C. *J. Org. Chem.* **1961**, *26*, 1831. (c) Kuwajima, I.; Ryochi, A.; Tomso, S. *Tetrahedron Lett.* **1983**, *24*, 4429. (d) Valades, L.; Siminez, M.; Rodreguez-Hahn, L. *Rev. Latinoam. Quim.* **1975**, *6*, 152. (e) Russell, G. A.; Makosza, M.; Hershberger, J. *J. Org. Chem.* **1979**, *44*, 1195. (f) Lampman, G. M.; Horne, D. A.; Hager, G. D. *J. Chem. Eng. Data* **1969**, *14*, 396.

(3) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron Lett.* **1988**, 987.

(4) *Carbenes*; Moss, R. A., Jones, M., Eds.; Wiley: New York, 1975; Vol. II; 1973; Vol. I. Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971.

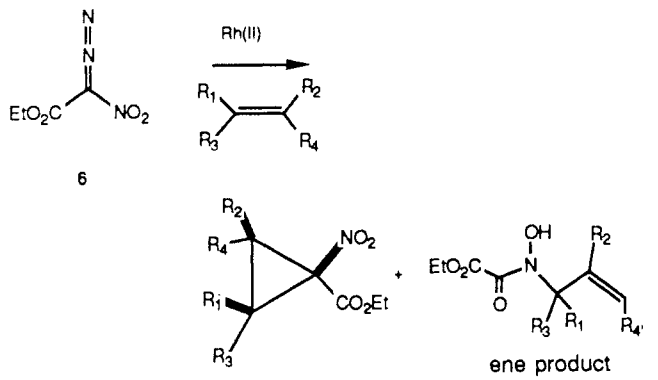
(5) (a) Schöllkopf, U.; Tonne, P. *Ann. Chem.* **1971**, *753*, 135. (b) Schöllkopf, U.; Markusch, P. *Ann. Chem.* **1971**, *753*, 143. (c) Schöllkopf, U.; Tonne, P.; Schaefer, H.; Markusch, P. *Ann. Chem.* **1969**, *722*, 45. (d) Frank-Neumann, M.; Miesch, M. *Tetrahedron Lett.* **1984**, 2909. (e) Rahman, A.; Clapp, L. *J. Org. Chem.* **1976**, *41*, 122. (f) Coutouli-Argyropoulou, E.; Alexandrou, N. E. *J. Org. Chem.* **1980**, *45*, 4158.

(6) For a review of metal carbene transformations, see: Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

(7) O'Bannon, P. E.; Carroll, P. J.; Dailey, W. P. *Tetrahedron Lett.* **1988**, 6031.

(8) 1-Alkylnitrocyclopropanes can be prepared by the methods of Shechter and Russell. See ref 2a and 2e.

**Scheme III**




| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| **13a** | H | H | Ph | H |
| **13b** | Ph | H | H | H |
| **13c** | H | Me | H | Me |
| **13d** | H | H | Me | Me |
| **13e** | Me | Me | H | H |
| **13f** | H | H | OAc | H |
| **13g** | OAc | H | H | H |
| **13h** | H | H | *n*-Bu | H |
| **13i** | *n*-Bu | H | H | H |
| **13j** | H | H | $-(CH_2)_4-$ | |
| **13k** | Me | H | Me | Me |
| **13l** | H | Me | Ph | H |
| **13m** | H | Ph | Me | H |
| **13n** | H | H | i-Pr | H |
| **13o** | H | H | t-Bu | H |
| **13p** | t-Bu | H | H | H |
| **14a** | Me | H | H | H |
| **14b** | Me | Me | H | H |
| **14c** | H | H | $-(CH_2)_3-$ | |

electrophile does not result in capture of the nitrocyclopropyl anion. Instead, only coupled products (**2** and **3**) could be isolated.[9] To circumvent this, they have developed methodology for the low-temperature nitration of cyclopropyl aryl ester enolates (**4**) (Scheme I).[10]

Our attempted cyclopropanation of 2,3-dimethyl-2-butene with ethyl nitrodiazoacetate (**6**) and catalyst afforded no cyclopropane. Instead, ethyl oxo[hydroxy-(1,1,2-trimethyl-2-propenyl)amino]acetate (**12**) was obtained in good yield.[11] This is the same product that Schöllkopf obtained when ethyl nitrodiazoacetate was pyrolyzed in the presence of the same alkene.[5a] Apparently, ethyl nitrodiazoacetate (**6**) undergoes nitrogen extrusion to form a nitrocarbene (**7**), which rearranges to an acyl nitroso compound (**8**) that reacts as an eneophile with the alkene. For nitrocarbene itself, this rearrangement is calculated to have no activation barrier and to be exothermic by 100 kcal/mol.[3] The intermediate acyl nitroso compound (**8**) can also be trapped as the Diels–Alder adduct **10** with 9,10-dimethylanthracene (Scheme II).[11]

## Results and Discussion

**Successful Cyclopropanation with Ethyl Nitrodiazoacetate.** Since our foiled attempt to cyclopropanate 2,3-dimethyl-2-butene with ethyl nitrodiazoacetate (**6**) in the presence of a catalytic amount of $Rh_2(OAc)_4$, we have carried out the reaction on a variety of alkenes and find that certain alkenes can be successfully cyclopropanated

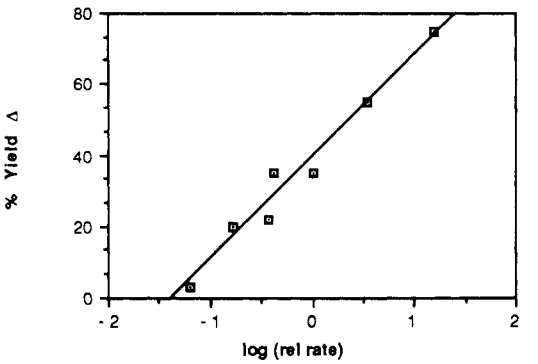
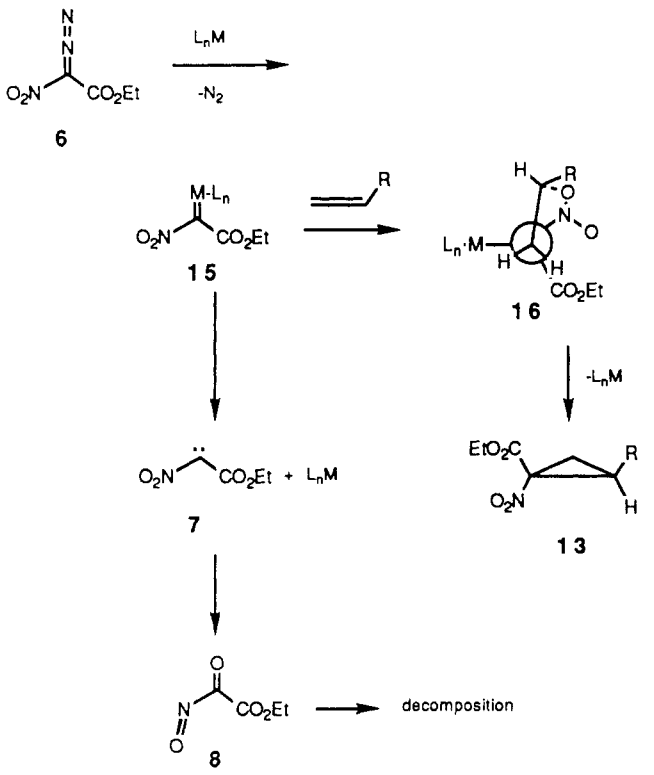



**Figure 1.** Percent yield of cyclopropane formation using catalytic rhodium(II) acetate and ethyl nitrodiazoacetate vs log (relative rate) of alkene based on 1-hexene.

**Scheme IV**




(Scheme III). The results are displayed in Table I. Cyclopropanes **13** are formed in yields ranging from 0 to 75%. Yields of ene products **14** span the same range. The course of the reaction is highly dependent on the substitution pattern of the alkene. Electron-rich and sterically undemanding alkenes give the best yields of cyclopropane products. As the alkene becomes more crowded, the yield of cyclopropanes decreases, and there is a concomitant increase in ene product.

In order to account for these results, we draw upon ideas advanced by Doyle.[12] In his model, the carbene moiety is transferred from an intermediate metal carbene (**15**) to the alkene via a $\pi$-complex (**16**) (Scheme IV). In the present case, we postulate that if the alkene is not sufficiently reactive, the nitrocarboethoxy carbene (**7**) dissociates from the metal and undergoes an irreversible rearrangement to an acyl nitroso compound (**8**), which reacts as an eneophile or decomposes unimolecularly to yield diethyl oxalate if no allylic hydrogens are accessible.[13]

(9) Kai, Y.; Knochel, P.; Kwiatkowski, S.; Dunitz, J. D.; Oth, J. F. M.; Seebach, D.; Kalinowski, H.-O. *Helv. Chim. Acta* **1982**, *65*, 137.
(10) Häner, R.; Maetzke, T.; Seebach, D. *Helv. Chim. Acta* **1986**, *69*, 1655.
(11) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron Lett.* **1988**, 5719.
(12) Doyle, M. P.; Giffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53.

Consistent with this hypothesis is the observation that yields of cyclopropane decrease as the reactant alkene is diluted with solvent.

**Competition Studies.** We desired to quantify these observations and correlate the yield of cyclopropane formation with alkene reactivity. A series of competition studies to determine the relative reactivities of several alkenes were performed. In Figure 1 percent yield of cyclopropane is plotted against the log of the relative reactivity of the alkenes. The degree of correlation is remarkable. Those alkenes with the highest relative rates give the best yields of cyclopropanes, and the least reactive give the poorest yield. Once again, this result is consistent with a labile metal nitrocarbenoid intermediate, which, in the absence of a suitably reactive alkene, undergoes irreversible rearrangement to an acyl nitroso compound and decomposes. These data and Doyle's data for ethyl diazoacetate are listed in Table I.

Of the alkenes studied, styrene is the most reactive toward both diazo compounds. With ethyl diazoacetate, it is 5 times more reactive than 3,3-dimethyl-1-butene, the least reactive alkene. This difference is widened to a factor of 250 with ethyl nitrodiazoacetate. The introduction of a nitro group onto the carbenic carbon will increase the electrophilicity of the intermediate carbenoid,[14] thereby making the nitrocarbethoxy carbenoid more sensitive to the electronic nature of the alkene than the unsubstituted carbethoxy carbenoid. Indeed, electron-rich alkenes such as styrene and vinyl acetate are more reactive toward the nitrocarbethoxy derivative than toward the parent carbethoxy carbenoid. Vinyl ethers, the most reactive alkenes toward ethyl diazoacetate, yield no isolable cyclopropanes with ethyl nitrodiazoacetate. In the reaction between ethyl vinyl ether and ethyl nitrodiazoacetate, only very polar uncharacterized material was obtained. Presumably, the incipient push–pull cyclopropane[15] is so destabilized by the combination of two very strongly electron-withdrawing groups with an excellent electron donor that it undergoes rapid ring opening and decomposes. In accord with this rationale is the observation that, of the above cyclopropanes, the vinyl acetate derivative is the least stable.

Curiously, while *cis*-2-butene gives moderate yields of cyclopropane with ethyl nitrodiazoacetate, *trans*-2-butene affords only the ene reaction product. Similarly, styrene has a relative reactivity of 17, yet *trans*-β-methylstyrene has a reactivity of 0.2. One also notes that relative to 1-hexene, cyclohexene, and 2-methyl-2-butene are less reactive toward ethyl nitrodiazoacetate but are more reactive with ethyl diazoacetate. Clearly, the nitrocarbethoxy carbenoid is also more sensitive to steric factors than the carbethoxy carbenoid. The nitro group will increase the size of the carbenoid, and the relative effectiveness of π-complex formation (hence the relative rate and the percentage of cyclopropanation) will now be more dependent upon the steric environment. Steric reasons may also explain why nitrodiazomethane cyclopropanates 2,3-dimethyl-2-butene while ethyl nitrodiazoacetate does not.

A log–log plot of the relative reactivities for the catalytic cyclopropanation of each diazo ester toward three alkyl monosubstituted alkenes is shown in Figure 2. The slope

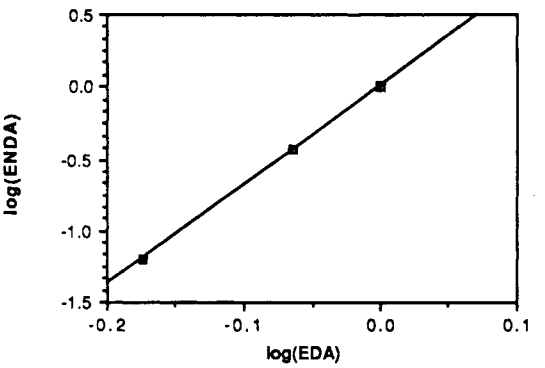
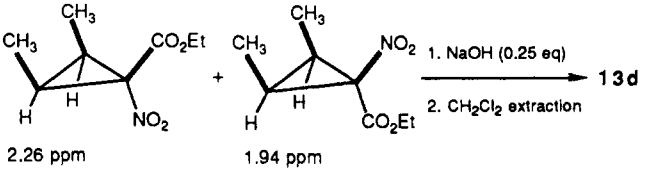
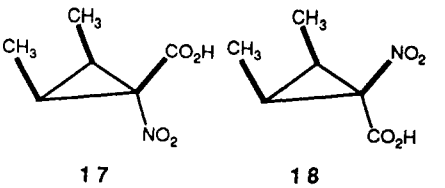



**Figure 2.** Plot of log (relative reactivity) based on 1-hexene for rhodium(II) acetate catalyzed cyclopropanation of alkyl monosubstituted alkenes with ethyl nitrodiazoacetate (ENDA) vs that with ethyl diazoacetate (EDA).

of the line is 6.91 with a correlation of 1.00. This suggests a similar mechanism involving an electrophilic metal carbene as the reactive intermediate in both reactions. Thus over this limited range, rhodium(II) acetate catalyzed cyclopropanation using ethyl nitrodiazoacetate is almost 7 times more sterically selective than that using ethyl diazoacetate as the substrate.

**Stereochemistry of Cyclopropanation.** Stereoselectivities for the $Rh_2(OAc)_4$-catalyzed cyclopropanation with both diazo compounds are given in Table I. In most cases cyclopropanation with ethyl nitrodiazoacetate gives greater diastereomeric excess than with ethyl diazoacetate. The ratio of geometric isomers was established on the basis of NMR spectra and corroborated by GC. In most cases the isomers could not be separated by column chromatography. The $^1H$ NMR spectra of mixtures of isomers showed two distinct sets of cyclopropyl hydrogens separated by 0.3 ppm. It was assumed that hydrogens syn to the nitro group which corresponds to the cis and major isomer would appear further downfield than hydrogens syn to the carboxylate group which corresponds to the trans and minor isomer. In most cases the minor and less hindered isomer could be separated from the major isomer through selective saponification.[16] For example, treating a 4:1 mixture of isomers **13d** and **13e** with 0.25 equiv of NaOH in ethanol/water afforded, after extraction of the basic aqueous layer with methylene chloride, the pure isomer **13d**. While this experiment, in conjunction with $^1H$ NMR data, supports the stereochemical assignment, confirmation came from X-ray structure data for the acid derivatives **17** and **18**.[17]



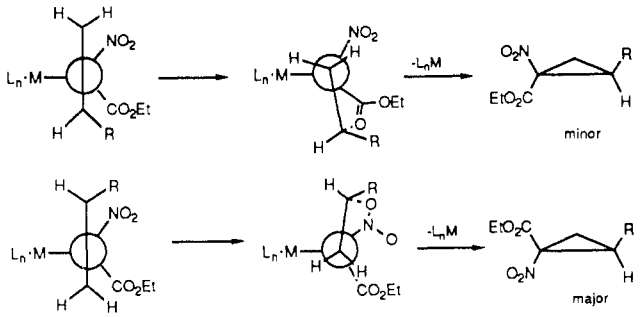

(13) Diethyl oxylate and diethyl carbonate are the major products in the pyrolysis of ethyl nitrodiazoacetate in inert solvents such as carbon tetrachloride and 1,2-dimethoxyethane (ref 5a).

(14) The nitro group is both a strong π- and σ-electron acceptor as shown by $\sigma_i = 0.65$ and $\sigma_r = 0.15$. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985.

(15) For a review of donor–acceptor-substituted cyclopropanes, see: Reissig, H.-U. In *Topics in Current Chemistry*; de Meijere, A., Ed.; Springer-Verlag: New York, 1988; Vol. 144.

(16) *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 913.

Scheme V




Ethyl nitrodiazoacetate not only gives greater diastereoselection than ethyl diazoacetate, but the cis isomer is obtained preferentially to the trans isomer. Generally, trans cyclopropanes predominate in rhodium(II) acetate cyclopropanations with diazocarboxylates. At first glance these data might seem to contradict Doyle's model. However, one would expect the oxygen atoms of the nitro group to stabilize the electrophilic β-carbon of the original alkene better than a carbonyl oxygen, thus resulting in the observed stereochemistry (Scheme V). It is interesting to note that when the very hindered alkene 3,3-dimethyl-1-butene is cyclopropanated, the stereochemical bias is reversed. That is, 3-methyl-1-butene affords a 1.3/1 cis/trans mixture of cyclopropanes, but 3,3-dimethyl-1-butene affords a 1/1.3 cis/trans mixture.

## Summary and Conclusions

The parent 1-nitrocyclopropanecarboxylate is the only previously synthesized example of this class of compounds. Its synthesis was accomplished through a low temperature nitration of the *o,o'*-di-*tert*-butyl-*p*-methoxyphenyl (DBHA) ester of cyclopropanecarboxylic acid. While our method is not without limitations, it does make this class of compounds much more accessible. The high degree of functionality present in these compounds should make them useful synthons for a variety of theoretically and biologically[18] interesting molecules. Seebach and Häner have demonstrated that these compounds may be converted to aminocyclopropanecarboxylates[19] and that they may be opened with nucleophiles. Subsequent reduction of the nitro group and cleavage of the ester affords free amino acids. Thus, these nitrocyclopropyl esters correspond to 2-aminobutanoic acid a[4] synthons.[20] Furthermore, in contrast to the DBHA esters, the ethyl esters can be hydrolyzed to nitrocyclopropyl carboxylic acids and reduced with lithium hydride to afford (nitrocyclopropyl)methanols.[21] Additional functionality can be introduced onto the cyclopropyl ring through correct choice of the initial alkene.

In summary, a simple one-step procedure for the synthesis of 1-nitrocyclopropanecarboxylates has been developed. The reaction works well with styrene and geminal and cis disubstituted alkenes. The cyclopropanes are formed with cis/trans ratios from 0.8 to 8.0. While the isomers are not easily separable, the cis isomer may be freed of the trans isomer through selective saponification in most cases. Trans and tetrasubstituted alkenes generally do not yield cyclopropanes.

(17) O'Bannon, P. E.; Carrol, P. J.; Dailey, W. P. *J. Struct. Chem.*, submitted for publication.
(18) Biological properties of cyclopropanes: Liu, H.-W.; Walsh, C. T. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987.
(19) Häner, R.; Seebach, D. *Chimia* **1985**, *39*, 356.
(20) (a) Seebach, D.; Häner, R.; Vettiger, T. *Helv. Chim. Acta* **1987**, *70*, 1507. (b) This nomenclature has been reveiwed: Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.
(21) O'Bannon, P. E.; Dailey, W. P., unpublished results.

## Experimental Section

**General Methods.** Proton magnetic resonance spectra were obtained in $CDCl_3$ with Bruker 250- and 500-MHz spectrometers. Chemical shifts are reported in δ units with $CHCl_3$ as an internal standard at 7.20 ppm. Carbon-13 magnetic resonance spectra were obtained with a Bruker 500-MHz spectrometer set at 125 MHz. Chemical shifts are reported in δ units with $CDCl_3$ as an internal standard at 77.0 ppm. High-resolution mass spectra were obtained on a VG-ZAB-E mass spectrometer under ammonia chemical ionization conditions. Infrared spectra were obtained on a Perkin-Elmer 1430 instrument and are reported for thin films. IR and mass spectral data are reported for mixtures of isomers. NMR data for the trans isomers are given for those cases where all absorbances could be unambiguously assigned. Analytical gas chromatographic analyses were obtained with an HP 5890A gas chromatograph using a 25-m methylsilicone capillary column and a flame ionization detector. Ethyl nitrodiazoacetate was prepared by the published procedure.[5c] All other reagents were used as supplied. **Caution**: While we have not experienced any problems handling ethyl nitrodiazoacetate, both nitrodiazomethane[3] and nitrodiazoacetic acid[7] have detonated with violent force on many occasions. Appropriate care should be exercised when handling any diazo compound.

**Catalytic Cyclopropanation Using Ethyl Nitrodiazoacetate.** Ethyl nitrodiazoacetate (1–10 mmol) was added to a stirred mixture of alkene (5–50 equiv) and rhodium(II) acetate (5 mol %) under argon and usually at room temperature at the rate of 5 mmol/h. After completion of addition, the mixture was stirred for 30 min. Excess alkene was evaporated, and the ene and cyclopropane products were separated by flash column chromatography (0–50% ether/hexane) with the cyclopropanes always eluting first. All the cyclopropane and ene products were isolated as oils.

**Selective Saponification of Ethyl *trans*-1-Nitrocyclopropanecarboxylates.** Once the isomeric composition had been determined by NMR or GC, 1.1 equiv of NaOH (based on amount of trans isomer) were added to a stirred solution of the mixture of 1-nitrocyclopropanecarboxylates in 1:1 ethanol/water. After being stirred at room temperature for 2 h, the mixture was extracted with methylene chloride, washed with brine, dried over magnesium sulfate, and concentrated to afford the pure cis isomer in 95% yield based on the amount of cis ester originally present in the mixture. This saponification reaction was not able to separate mixtures of ethyl 1-nitrocyclopropanecarboxylates derived from vinyl acetate or β-methylstyrene.

**Competitive Catalytic Cyclopropanation Reactions with Ethyl Nitrodiazoacetate.** Ethyl nitrodiazoacetate (0.1 mmol) was added over 10 min to a stirred mixture of alkenes (usually a 1:1 mol ratio; minimum amount 10 equiv) and catalyst. After the mixture was stirred for 15 min, excess alkene was evaporated and the reaction mixture was subjected to GC analysis. Relative response factors were determined by using known mixtures of authentic cyclopropanes. When cross comparisons of the reactivity of alkenes allowed more than one estimate of reactivity, the results agreed to within 15%.

**Ethyl 1-Nitro-*cis*-2-phenylcyclopropanecarboxylate (13a).** $^1H$ NMR: δ 0.84 (t, $J$ = 7.1 Hz, 3 H), 2.14 (dd, $J$ = 10.7, 8.6 Hz, 1 H), 2.39 (dd, $J$ = 9.1, 8.6 Hz, 1 H), 3.71 (dd, $J$ = 10.7, 9.1 Hz, 1 H), 3.91 (q, $J$ = 7.1 Hz, 2 H), 7.25 (m, 5 H). IR 1750, 1550 $cm^{-1}$. HR-MS: $(M + H^+)$ 236.0908, calcd for $C_{12}H_{14}NO_4$ 236.0925.

**Ethyl 1-Nitro-*trans*-2-phenylcyclopropanecarboxylate (13b).** $^1H$ NMR: δ 1.28 (t, $J$ = 7.2 Hz, 3 H), 1.96 (dd, $J$ = 9.9, 6.9 Hz, 1 H), 2.62 (dd, $J$ = 9.2, 6.9 Hz, 1 H), 3.42 (dd, $J$ = 9.7, 9.2 Hz, 1 H), 4.29 (q, $J$ = 7.2 Hz, 2 H), 7.26 (m, 5 H).

**Ethyl 2,2-Dimethyl-1-nitrocyclopropanecarboxylate (13c).** $^1H$ NMR: δ 1.15 (s, 3 H), 1.21 (t, $J$ = 7.2 Hz, 3 H), 1.29 (s, 3 H), 1.63 (d, $J$ = 6.6 Hz, 1 H), 1.79 (d, $J$ = 6.6 Hz, 1 H), 4.15 (q, $J$ = 7.2 Hz, 2 H). $^{13}C$ NMR: δ 13.9, 19.7, 22.4, 28.7, 30.9, 62.6, 75.6, 164.6. IR 1730, 1540, 1340 $cm^{-1}$. HR-MS: $(M + H^+)$ 188.0908, calcd for $C_8H_{14}NO_4$ 188.0925.

**Ethyl *cis,cis*-2,3-Dimethyl-1-nitrocyclopropanecarboxylate (13d).** $^1H$ NMR: δ 1.14 (m, 6 H), 1.26 (t, $J$ = 7.0 Hz, 3 H), 2.26 (m, 2 H), 4.25 (q, $J$ = 7.0 Hz, 2 H). $^{13}C$ NMR: δ

8.3, 13.9, 28.8, 62.2, 72.8, 162.2. IR 1750, 1540, 1340 $cm^{-1}$. HR-MS ($M + NH_4^+$) 205.1188, calcd for $C_8H_{17}N_2O_4$ 205.1182.

**Ethyl *trans*,*trans*-2,3-Dimethyl-1-nitrocyclopropanecarboxylate (13e).** $^1H$ NMR: $\delta$ 1.14 (m, 6 H), 1.21 (t, $J$ = 7.2 Hz, 3 H), 1.94 (m, 2 H), 4.17 (q, $J$ = 7.2 Hz, 2 H). $^{13}C$ NMR: $\delta$ 8.5, 13.9, 26.8, 62.8, 73.4, 166.7.

**Ethyl *cis*-2-Acetoxy-1-nitrocyclopropanecarboxylate (13f).** $^1H$ NMR: $\delta$ 1.24 (t, $J$ = 7.0 Hz, 3 H), 1.99 (s, 3 H), 2.18 (d, $J$ = 7.5 Hz, 2 H), 4.25 (q, $J$ = 7.0 Hz, 2 H), 5.07 (t, $J$ = 7.5 Hz, 1 H). $^{13}C$ NMR: $\delta$ 13.8, 20.2, 21.9, 56.8, 63.1, 68.4, 160.7, 169.5. IR 1750, 1550, 1360 $cm^{-1}$. HR-MS: ($M + NH_4^+$) 235.095, calcd for $C_8H_{18}N_2O_6$ 235.0931.

**Ethyl *trans*-2-Acetoxy-1-nitrocyclopropanecarboxylate (13g).** $^1H$ NMR: $\delta$ 1.23 (t, $J$ = 7.3 Hz, 3 H), 1.92 (dd, $J$ = 8.6, 7.5 Hz, 1 H), 1.99 (s, 3 H), 2.34 (dd, $J$ = 8.6, 5.9 Hz, 1 H), 4.21 (q, $J$ = 7.3 Hz, 2 H), 4.85 (dd, $J$ = 7.5, 5.9 Hz, 1 H). $^{13}C$ NMR: $\delta$ 13.8, 20.3, 20.6, 55.2, 63.3, 68.4, 163.8, 169.5.

**Ethyl *cis*-2-*n*-Butyl-1-nitrocyclopropanecarboxylate (13h).** $^1H$ NMR: $\delta$ 0.82 (t, $J$ = 7.1 Hz, 3 H), 1.2 (m, 9 H), 1.58 (dd, $J$ = 8.9, 6.1 Hz, 1 H), 1.78 (dd, $J$ = 10.5, 6.1 Hz, 1 H), 2.35 (m, 1 H), 4.25 (q, $J$ = 7.1 Hz, 2 H). $^{13}C$ NMR: $\delta$ 13.8, 13.9, 22.1, 23.0, 27.5, 30.3, 30.6, 62.6, 70.5, 163.5. IR 1750, 1550 $cm^{-1}$. HR-MS: ($M + NH_4^+$) 233.1501, calcd for $C_{10}H_{21}N_2O_4$ 233.1508.

**Ethyl *trans*-2-*n*-Butyl-1-nitrocyclopropanecarboxylate (13i).** $^1H$ NMR: $\delta$ 0.82 (t, $J$ = 7.1 Hz, 3 H), 1.2 (m, 9 H), 1.62 (dd, $J$ = 12.8, 6.2 Hz, 1 H), 1.76 (dd, $J$ = 8.5, 6.2 Hz, 1 H), 2.05 (m, 1 H), 4.22 (q, $J$ = 7.1 Hz, 2 H). $^{13}C$ NMR: $\delta$ 13.6, 13.7, 22.0, 22.1, 27.7, 29.0, 30.2, 62.6, 71.4, 165.8.

**Ethyl *syn*-7-Nitrobicyclo[4.1.0]heptane-7-carboxylate (13j).** $^1H$ NMR: $\delta$ 1.05 (m, 2 H), 1.23 (m, 2 H), 1.30 (t, $J$ = 7.2 Hz, 3 H), 1.88 (m, 4 H), 2.30 (m, 2 H), 4.29 (q, $J$ = 7.2 Hz, 2 H). $^{13}C$ NMR: $\delta$ 13.8, 19.1, 20.2, 28.4, 62.3, 72.0, 162.0. IR 1750, 1550 $cm^{-1}$. HR-MS: ($M + H^+$) 214.1075, calcd for $C_{10}H_{16}NO_4$ 214.1082.

**Ethyl 2,2-Dimethyl-*cis*-3-methyl-1-nitrocyclopropanecarboxylate (13k).** $^1H$ NMR: $\delta$ 1.11 (d, $J$ = 6.6 Hz, 3 H), 1.15 (s, 3 H), 1.23 (t, $J$ = 7.1 Hz, 3 H), 1.30 (s, 3 H), 2.17 (q, $J$ = 6.6 Hz, 1 H), 4.19 (q, $J$ = 7.1 Hz, 2 H). IR 1750, 1550 $cm^{-1}$. HR-MS: ($M + H^+$) 202.1079, calcd for $C_9H_{16}NO_4$ 202.1082.

**Ethyl 1-Nitro-*trans*-3-methyl-*cis*-2-phenylcyclopropanecarboxylate (13l).** $^1H$ NMR: $\delta$ 1.12 (t, $J$ = 7.3 Hz, 3 H), 1.36 (d, $J$ = 6.7 Hz, 3 H), 2.52 (dq, $J$ = 11.3, 6.7 Hz, 1 H), 3.58 (d, $J$ = 11.3 Hz, 1 H), 4.13 (q, $J$ = 7.3 Hz, 2 H), 7.3 (m, 5 H). IR 1740, 1540 $cm^{-1}$. HR-MS: ($M + H^+$) 250.105, calcd for $C_{13}H_{16}NO_4$ 250.1082.

**Ethyl 1-Nitro-*cis*-3-methyl-*trans*-2-phenylcyclopropanecarboxylate (13m).** $^1H$ NMR: $\delta$ 0.88 (t, $J$ = 7.2 Hz, 3 H), 1.28 (d, $J$ = 6.4 Hz, 3 H), 2.68 (dq, $J$ = 9.2, 6.4 Hz, 1 H), 3.47 (d, $J$ = 9.2 Hz, 1 H), 3.91 (q, $J$ = 7.2 Hz, 2 H), 7.3 (m, 5 H).

**Ethyl *cis*-2-Isopropyl-1-nitrocyclopropanecarboxylate (13n).** $^1H$ NMR: $\delta$ 0.97 (d, $J$ = 2.4 Hz, 3 H), 1.00 (d, $J$ = 2.5 Hz, 3 H), 1.16 (m, 1 H), 1.27 (t, $J$ = 7.2 Hz, 3 H), 1.62 (dd, $J$ = 9.1, 5.9 Hz, 1 H), 1.75 (dd, $J$ = 10.6, 5.9 Hz, 1 H), 2.19 (ddd, $J$ = 10.6, 9.1, 9.4 Hz, 1 H), 4.27 (q, $J$ = 7.2 Hz, 2 H). IR 1740, 1540 $cm^{-1}$. HR-MS: ($M + H^+$) 202.107, calcd for $C_9H_{16}NO_4$ 202.1082.

**Ethyl *cis*-2-*tert*-Butyl-1-nitrocyclopropanecarboxylate (13o).** $^1H$ NMR: $\delta$ 0.93 (s, 9 H), 1.32 (t, $J$ = 7.3 Hz, 3 H), 1.70 (d, $J$ = 10.0 Hz, 2 H), 2.42 (t, $J$ = 10.0 Hz, 1 H), 4.28 (q, $J$ = 7.1 Hz, 2 H). IR 1740, 1540 $cm^{-1}$. HR-MS: ($M + H^+$) 216.125, calcd for $C_{10}H_{18}NO_4$ 216.1231.

**Ethyl *trans*-2-*tert*-Butyl-1-nitrocyclopropanecarboxylate (13p).** $^1H$ NMR: $\delta$ 0.92 (s, 9 H), 1.26 (t, $J$ = 7.3 Hz, 3 H), 1.55 (dd, $J$ = 10.1, 6.1 Hz, 1 H), 2.02 (t, $J$ = 10.1 Hz, 1 H), 4.21 (q, $J$ = 7.3 Hz, 2 H).

**Ethyl Oxo[hydroxy(1-methyl-2-propenyl)amino]acetate (14a) (1:1 mixture of rotamers).** $^1H$ NMR: $\delta$ 1.13-1.34 (m, 4.5 H), 1.37-1.47 (m, 1.5 H), 4.22-4.34 (m, 2 H), 4.87-4.97 (m, 1 H), 5.14-5.24 (m, 2 H), 5.75-5.97 (m, 1 H), 7.6 (br, 1 H). $^{13}C$ NMR: $\delta$ 13.9, 15.6, 17.4, 53.5, 57.8, 62.5, 63.0, 117.3, 117.5, 135.1, 135.5, 154.3, 160.0, 160.7, 163.3. IR 3200, 1750, 1650 $cm^{-1}$. HR-MS: ($M + H^+$) 188.0923, calcd for $C_8H_{14}NO_4$ 188.0925.

**Ethyl Oxo[hydroxy(1,2-dimethyl-2-propenyl)amino]acetate (14b) (1:1 mixture of rotamers).** $^1H$ NMR: $\delta$ 1.31-1.40 (m, 4.5 H), 1.50-1.57 (m, 1.5 H), 1.74 (s, 3 H), 4.23-4.38 (m, 2 H), 4.77-4.83 (m, 0.5 H), 4.87-4.95 (m, 0.5 H), 4.99-5.03 (m, 2 H), 7.6 (br, 1 H). $^{13}C$ NMR: $\delta$ 13.8, 14.4, 15.9, 20.0, 20.4, 55.4, 59.9, 62.4, 63.0, 113.6, 113.8, 142.2, 154.2, 160.2, 160.9, 163.3. IR 3200, 1750, 1650 $cm^{-1}$. HR-MS: ($M + H^+$) 202.1075, calcd for $C_9H_{16}NO_4$ 202.1082.

**Ethyl Oxo[hydroxy(2-cyclohexenyl)amino]acetate (14c) (1:1 mixture of rotamers).** $^1H$ NMR: $\delta$ 1.22-1.31 (m, 3 H), 1.51-1.59 (m, 1 H), 1.75-2.02 (m, 5 H), 4.20-4.27 (m, 2 H), 4.62 (br, 0.5 H), 4.88 (br, 0.5 H), 5.43-5.50 (m, 1 H), 5.88-5.91 (m, 1 H), 8.2 (br, 1 H). $^{13}C$ NMR: $\delta$ 20.7, 20.8, 24.1, 24.3, 25.4, 26.7, 27.8, 27.9, 52.2, 56.6, 84.9, 85.2, 124.7, 124.8, 132.9, 133.1, 155.8, 159.8, 161.2, 163.0. IR 3200, 1750, 1650 $cm^{-1}$. HR-MS: ($M + H^+$) 214.1079, calcd for $C_{10}H_{16}NO_4$ 214.1082.

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# Oxidation Potentials of Carbanions and Homolytic Bond Dissociation Energies of Their Conjugate Acids

F. G. Bordwell,* John A. Harrelson, Jr., and A. V. Satish

*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208*

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Oxidation potentials for carbanions derived from hydrocarbons and representative carbonyl, cyano, and nitro compounds have been measured in $Me_2SO$ solution by cyclic voltammetry. The problem of referencing these values to the aqueous standard hydrogen electrode, $SHE_{aq}$, which is necessary in order to estimate homolytic bond dissociation energies (BDEs) in $Me_2SO$, is discussed. The $E_{ox}(A^-)$ values for the enolate ions derived from acetylacetone and diethyl malonate with $Li^+ClO_4^-$ as an electrolyte have been found to be 0.52 and 0.45 V more positive, respectively, than those using a $Et_4N^+BF_4^-$ electrolyte due to the stabilizing influence of the $Li^+$ ion in the lithium chelate. Oxidation potentials for the delocalized carbanions derived from nine hydrocarbons have been found to plot linearly with the equilibrium acidities of their conjugate acids. The slope is near unity but the plot exhibits considerable scatter ($R^2$ = 0.94), and points for 10 other hydrocarbons giving delocalized anions were found to deviate substantially from the line. The BDE estimated from the $pK_{HA}$ and $E_{ox}(A^-)$ values for the acidic C-H bond in 6,6-dimethylfulvene (84.5 kcal/mol) is considerably above the average for the group of nine (81) and that for 9,10-dihydroanthracene is below average (78). The BDE for the latter, as well as the BDEs for toluene and propene, are within our experimental error of the corresponding gas-phase values. The BDE estimated from the acidic C-H bond in 1,1,3,3-tetraphenylpropene is 8 kcal/mol lower than that in propene.

Oxidation potentials in $Me_2SO$ for carbanions generated from hydrocarbons or their derivatives have been (a) correlated with the acidities of their conjugate acids,[1,2] (b) related to rates of nonchain single-electron transfer (SET)

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