# Cobalt-Mediated Synthesis of Nitro Enones from 1,3-Dienes and Alkylnitronates

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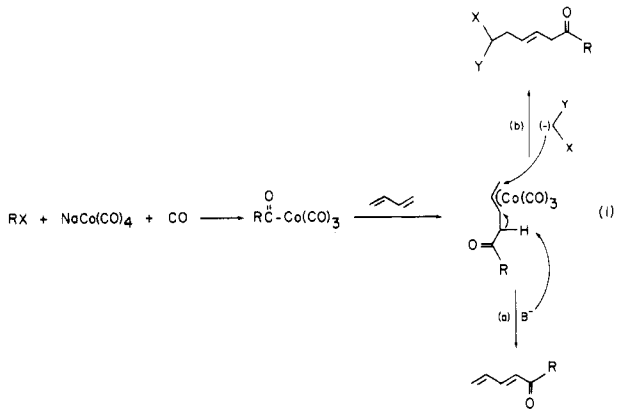
Nitronate anions react with ($\pi$-allyl)cobalt complexes produced from the acylation of 1,3-dienes by acetylcobalt tetracarbonyl to produce nitro enones. With sterically hindered nitronates or ($\pi$-allyl)cobalt species, elimination to form the dienone is a competing process. Allenes undergo a similar process.

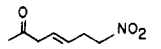
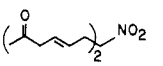
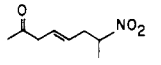
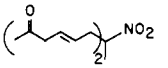
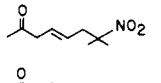
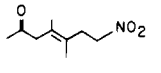
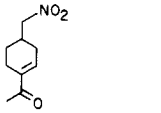
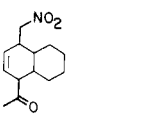
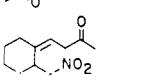
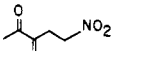
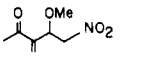
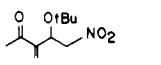
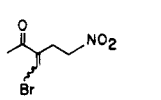
Acylcobalt carbonyl complexes, prepared from $NaCo(CO)_4$ and reactive organic halides, react with 1,3-dienes to produce acylated ($\pi$-allyl)cobalt complexes by insertion of the diene into the cobalt-acyl carbon bond. With unsymmetrical dienes, acylation always occurs at the less substituted terminus. As substitution on the diene increases, the acylation process becomes less efficient. In the acylated ($\pi$-allyl)cobalt complexes, the protons $\alpha$ to both the $\pi$-allyl group and the carbonyl group are acidic and undergo facile abstraction by bases to produce the acyldiene in good yield (eq 1).[1] We previously reported[2] the alkylation of acylated ($\pi$-allyl)cobalt complexes by stabilized carbanions such as malonate, acetoacetate, and cyanoacetate (eq 1). Herein we report the extension of this process to the use of alkylnitronates (nitroalkyl carbanions) as nucleophiles to convert dienes to nitro enones.




## Results and Discussion

Initial attempts to extend the cobalt-mediated 1,4 disubstitution of 1,3-dienes to a wider range of nucleophiles were unsuccessful. Anions such as phenoxide, thiophenoxide, cyanide, and benzamide, and the free amine, pyrrolidine, caused elimination to form the dienone (eq 1, path a) rather than addition (eq 1, path b). In contrast aniline did not react at all, and azide and malononitrile anions produced intractable mixtures of unidentified organic products. Under conditions reported[2] for the successful alkylation of these complexes by malonate anion (THF, 25 °C) nitromethane anion failed to react at all. However, this lack of reactivity was likely due to the insolubility of nitromethane anion in THF. Generation of this anion in $Me_2SO$, in which it is soluble, and addition of this solution to a THF solution of the acylated ($\pi$-allyl)cobalt complex resulted in alkylation and the production of nitro enone in reasonable yield (eq 2). The results of this reaction using a variety of dienes and alkyl nitronates are summarized in Table I.

**Table I. Acylation/Nitroalkylation of 1,3-Dienes**

| diene | anion | product | yield,[a,b] % |
|---|---|---|---|
|  |  |  | 25 |
| | |  | 26 |
|  |  |  | 43 |
| | |  | 29 |
|  |  |  | 64 |
|  |  |  | 10[c] |
|  |  |  | 74 |
|  |  |  | 54 |
|  |  |  | 20[d] |
|  |  |  | 48 |
|  |  |  | 35 |
|  |  |  | 8 |
|  |  |  | 7 |

[a] Yields are based on initial amount of cobalt anion used. [b] Yields are for isolated, purified material. [c] Dienone (23%) was also obtained. [d] Dienone (46%) was also obtained.

Butadiene was efficiently converted to the corresponding nitro enone when treated with alkylnitronates. Nitromethane and nitroethane produced substantial amounts of dialkylation products as is typical for carbanions having several acidic protons.[2,3] Exclusive alkylation at the less

(1) (a) Heck, R. F. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1968; Vol. I, pp 388–397. (b) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3381. (c) *Ibid.* **1963**, *85*, 3383. (d) *Ibid.* **1963**, *85*, 3387.

(2) Hegedus, L. S.; Inoue, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4917 and references cited therein.

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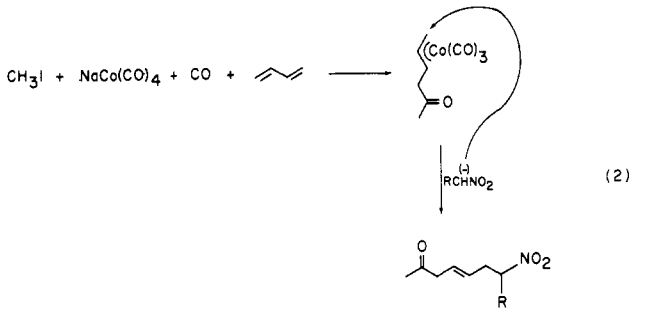
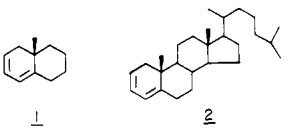



(2)

substituted terminus of the $\pi$-allyl system by the carbon atom of the nitronate was observed.[4] 2,3-Dimethylbutadiene was much less efficient in this process, producing nitro enone in only 10% yield. This was accompanied by dienone (23%) from elimination rather than alkylation. The low overall yield reflects the poor conversion of the sterically hindered diene to the acylated ($\pi$-allyl)cobalt species.[1]

Cyclohexadiene was also efficiently converted to the nitro enone when nitromethane anion was the nucleophile. In this single case, the double bond in the product rearranged into conjugation with the carbonyl group. In contrast, the more sterically hindered anion of 2-nitropropane effected elimination to form the dienone (87%) rather than alkylation. Decalin-1,3-diene also was alkylated in reasonable yield by nitromethane anion. The sterically more congested dienes 1 and 2 underwent ex-



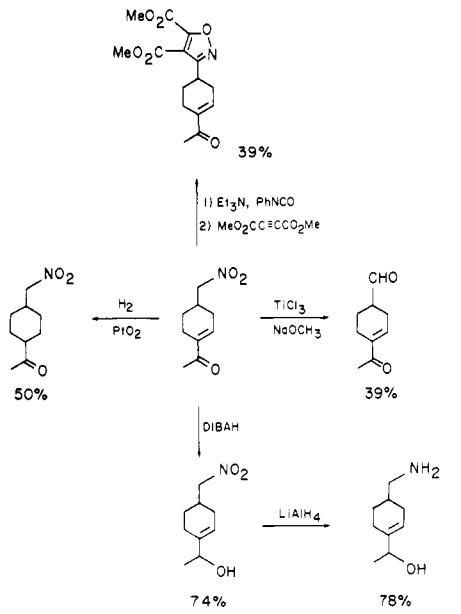
1 2

clusive elimination to form the corresponding acyldiene rather than the desired nitro enone. As usual, acylation occurred at the less substituted end of the diene. 1-Vinylcyclohexene was acylated at the less substituted diene terminus and alkylated in low yield by nitromethane anion. Again, a substantial amount of the dienone (46%) from competitive elimination was obtained.

Allenes react with acylcobalt species to produce [$\pi$-(2-acylallyl)]cobalt complexes. The complex from allene itself was converted to the nitro enone by nitromethane anion in fair yield. In contrast to the product resulting from malonate anion,[2] further conjugate addition of the nitromethane anion to the conjugated enone product did not occur. Substituted allenes also were reactive in this system. Remarkably, 1-methoxyallene was alkylated exclusively at the more substituted, more electron-rich end of the $\pi$-allyl group. Similarly, the very hindered 1-*tert*-butoxyallene also was alkylated exclusively at the alkoxy-bearing terminus of the $\pi$-allyl system, albeit, in very low yield. In contrast, 1-bromoallene underwent alkylation at the less substituted site, again in very low yield. In these cases, there appears to be an electronic bias controlling the site of alkylation, directing it to the most electron-rich site of the $\pi$-allyl complex.

The nitro enones produced above are highly functionalized molecules, and undergo reaction typical of the functional groups present (Scheme I). They are available from a one-pot reaction, from simple starting materials,

**Scheme I**




using standard laboratory glassware, in fair to good yield.

## Experimental Section

**General Procedures.** Melting points were taken with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Acculab 3 or Beckman 4240 spectrometer. $^1$H NMR spectra were recorded with a Varian T-60 (60 MHz), Varian EM360A (60 MHz), or a Nicolet NTCFT 1180 (360 MHz) spectrometer with tetramethylsilane as an internal standard. Liquid chromatography was performed by using a radial layer chromatographic device (Chromatotron, Harrison Research) with plates of Kiesel gel 60 PF254 silica gel or under moderate pressures (20–50 psi) with Merck silica gel 60 (40–60 $\mu$m). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. All manipulations of cobalt complexes were carried out under an argon atmosphere.

**Materials.** The complex $NaCo(CO)_4$ was synthesized from $Co_2(CO)_8$ and solid NaOH[5] in THF. The cobalt anion was then dried over excess NaH for 4 h and then filtered. The concentration of cobalt tetracarbonyl anion in THF was determined by adding excess $I_2$ to the solution and then measuring the carbon monoxide evolved by a gasometric procedure.[6] THF was distilled from sodium/benzophenone. Butadiene (Matheson), 2,3-dimethyl-1,3-butadiene (Aldrich), 1,3-cyclohexadiene (Matheson), $Me_2SO$ (Fischer), $I_2$ (Fischer), allene (ICN), and 2-nitropropane (Alfa) were used as received. Methyl iodide, nitromethane, and nitroethane were distilled before use.

**Preparation of Nitronate Anions.** Sodium hydride (50% mineral oil suspension, Aldrich) was washed two to three times with dry hexane or petroleum ether under an argon atmosphere. Most of the solvent was removed via syringe. The remaining solvent was removed under reduced pressure. The carbanion solution was made by adding $Me_2SO$ to the dry NaH followed by the appropriate amount of nitroalkane. The anion was allowed to form at room temperature for 2–8 h.

**Preparation of Cobalt $\pi$-Allyl Species.** THF was placed in a dry Airlessware flask filled with argon. To this was added the titrated $NaCo(CO)_4$ solution via syringe. Methyl iodide was then introduced followed by the appropriate diene. Stirring continued at room temperature for 2–10 h as noted. Formation of the $\pi$-allyl species was followed by IR. The appearance of bands at 1980 and 2045 cm$^{-1}$ indicated a $\pi$-allyl species present. Starting material ($NaCo(CO)_4$) appeared at 1850 and 1880 cm$^{-1}$.[1b]

When no starting material was observed or the amount of starting material failed to decrease significantly, the nucleophile

(3) Polyalkylation of nitronate anions had also been observed in the Pd-catalyzed telomerization of butadiene: Tsuji, J.; Yamakawa, T.; Mandai, T. *Tetrahedron Lett.* **1978**, 565. Tsuji, J.; Mandai, T., *Ibid.* **1980**, *21*, 3285.

(4) Nitronates often undergo O-alkylation rather than C-alkylation: Kornblum, N. *Synthesis* **1975**, 734. Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1.

(5) Hieber, W.; Sedlmeier, J.; Abeck, W. *Chem. Ber.* **1953**, *86*, 700.

(6) Sternberg, H. W.; Wender, I.; Orchin, M. *Anal. Chem.* **1952**, *24*, 174.

was added via a cannula and the reaction placed under an atmosphere of carbon monoxide.

**Product Isolation.** The contents of the flask were diluted with diethyl ether and poured into a seperatory funnel. The reaction was quenched by washing the mixture two times with a saturated $NH_4Cl$ solution. Then excess $I_2$ in ether was added to decompose any cobalt carbonyl species remaining. The solution was shaken until the brown color of iodine persisted for 0.25–0.5 h. The brown solution was washed twice with brine and the excess $I_2$ reduced by washing two times with a saturated aqueous solution of $Na_2S_2O_3$. The organic layer was washed twice with water and dried over $MgSO_4$ and the solvent removed in vacuo.

**Preparation of Dienes.** *cis*-Decalin-1,3-diene was prepared by the method of Jacobson,[7] and 6-methyldecalin-1,3-diene was made as described by Shapiro et al.[8] while $\Delta^{2,4}$-cholestadiene was synthesized according to Mandell.[9] 1-Vinyl-1-cyclohexene was prepared as described by Pleshakov.[10] Methoxyallene was prepared by a known method[11] as was *tert*-butoxyallene[12] and bromoallene.[13]

***trans*-Nitrohept-3-en-6-one.** The $\pi$-allyl complex was formed over 4 h [4.00 mL of 0.53 M $NaCo(CO)_4$ (2.12 mmol), 140 $\mu$L of $CH_3I$ (2.25 mmol), 15 mL of THF, excess 1,3-butadiene bubbled into solution]. The nitromethane anion was then added [230 $\mu$L of $CH_3NO_2$ (4.25 mmol), 108 mg of NaH (50%, 4.25 mmol), 15 mL of $Me_2SO$, stir 4 h]. The orange solution turned deep yellow, then orange, red, and yellow-orange over 5 min. The reaction continued 4 h, and after the standard isolation, column chromatography (1:1 hexane/ethyl acetate) gave 83 mg (25%, $R_f$ 0.42) of product as a light yellow oil: $^1H$ NMR ($CDCl_3$) $\delta$ 2.13 (s, 3, $COCH_3$), 2.72 (q, $J$ = 6.7 Hz, 2, $=CHCH_2CH_2NO_2$), 3.13 (d, $J$ = 6.5 Hz, 2, $COCH_2CH=$), 4.40 (m, 2 $CH_2NO_2$), 5.59 (m, 2, CH=CH); IR (neat) 1720 (C=O), 1555 ($CNO_2$), 1382, 1363 ($CNO_2$), 970 (CH=CH, trans) $cm^{-1}$. An analytical sample was obtained by evaporative distillation. Anal. ($C_7H_{11}NO_3$) C, H, N.

In addition, 73 mg (26%, $R_f$ 0.17) of 2,12-dioxo-7-nitro-*trans,trans*-4,9-tridecadiene was obtained: $^1H$ NMR ($CDCl_3$) $\delta$ 2.13 (s, 6, $COCH_3$), 2.65 (d, $J$ = 6 Hz, 4, $=CHCH_2CHNO_2$), 3.15 (d, $J$ = 6 Hz, 4, $COCH_2CH=$), 4.52 (q, $J$ = 6 Hz, 1, $CHNO_2$), 5.56 (m, 4, CH=CH); IR (neat) 1720 (C=O), 1550 ($CNO_2$), 1362 ($CNO_2$), 978 (CH=CH, trans) $cm^{-1}$. Evaporative distillation gave a analytical sample. Anal. ($C_{13}H_{19}NO_4$) C, H, N.

***trans*-2-Nitrooct-4-en-7-one.** The $\pi$-allyl complex was formed over 9 h [5.00 mL of 0.57 M $NaCo(CO)_4$ (2.85 mmol), 200 $\mu$L of $CH_3I$ (3.2 mmol), 15 mL of THF, excess 1,3-butadiene] and was followed by addition of the nitroethane anion [431 $\mu$L of $CH_3CH_2NO_2$ (6.0 mmol), 280 mg of NaH (50%, 6.0 mmol), 20 mL of $Me_2SO$, stir 8 h]. The solution turned pea-green, then yellow, orange, and red over 3 min. The reaction continued for 12.2 h. The usual isolation and separation by Chromatotron (2:1 hexane/ethyl acetate) gave 250 mg (50%, $R_f$ 0.33) of product as a yellow oil: $^1H$ NMR ($CDCl_3$) $\delta$ 1.57 (d, $J$ = 7 Hz, 3, $CH_3CHNO_2$), 2.13 (s, 3, $CH_3CO$), 2.52 (m, 2, $=CHCH_2CNO_2$), 3.05 (d, $J$ = 6 Hz, 2, $COCH_2CH=$), 4.48 (q, $J$ = 6 Hz, 1, $CH_3CH(NO_2)$), 5.53 (m, 2, CH=CH); IR ($CHCl_3$) 1718 (C=O), 1545 ($CNO_2$), 1361 ($CNO_2$), 970 (CH=CH, trans) $cm^{-1}$. Evaporative distillation (60 °C/0.025 mm) gave an analytical sample. Anal. ($C_8H_{13}NO_3$) C, H, N.

The bisalkylated product 2,12-dioxo-7-methyl-7-nitro-*trans,trans*-4,9-tridecadiene was also obtained (110 mg, 29%, $R_f$ = 0.18) as a yellow liquid: $^1H$ NMR ($CDCl_3$) $\delta$ 1.51 (s, 3, $CH_3CNO_2$), 2.13 (s, 6, $CH_3CO$), 2.61 (m, 4, $=CHCH_2CNO_2$), 3.15 (d, $J$ = 6 Hz, 4, $COCH_2CH=$), 5.53 (m, 4, CH=CH); IR ($CHCl_3$) 1718 (C=O), 1538 ($CNO_2$), 1359 ($CNO_2$), 971 (CH=CH, trans) $cm^{-1}$. Evaporative distillation gave an analytical sample. Anal. ($C_{17}H_{21}NO_4$) C, H, N.

***trans*-2-Methyl-2-nitrooct-4-en-7-one.** The $\pi$-allyl species was made as usual over 8.7 h [5.00 mL of 0.589 M $NaCo(CO)_4$ (2.94 mmol), 200 $\mu$L of $CH_3I$ (32 mmol), 15 mL of THF, excess 1,3-butadiene]. The 2-nitropropane anion was added [288 $\mu$L of 2-nitropropane (3.2 mmol), 154 mg of NaH (50%, 3.2 mmol), 40 mL of $Me_2SO$, stir 7 h] and allowed to react for 16 h. Initially the mixture turned bright yellow then slowly turned deep red. The usual isolation with Chromatotron purification (1:1 hexane/ethyl acetate) gave 348 mg (64%, $R_f$ 0.44) of product: $^1H$ NMR ($CDCl_3$) $\delta$ 1.54 (s, 6, $(CH_3)_2CNO_2$), 2.03 (s, 3, $CH_3CO$), 2.55 (d, $J$ = 6 Hz, 2, $=CHCH_2CNO_2$), 3.06 (d, $J$ = 6 Hz, 2, $COCH_2CH=$), 5.45 (m, 2, CH=CH); IR (neat) 1719 (C=O), 1535 ($CNO_2$), 1350 ($CNO_2$), 971 (HC=CH, trans) $cm^{-1}$. An analytical sample was obtained by evaporative distillation (105 °C (0.075 mm)). Anal. ($C_9H_{15}NO_3$) C, H, N.

***trans*-3,4-Dimethyl-1-nitrohept-3-en-6-one.** The $\pi$-allyl complex was formed over 4 h [4.00 mL of 0.726 M $NaCo(CO)_4$ (2.90 mmol), 20 mL of THF, 200 $\mu$L of $CH_3I$ (3.1 mmol), 750 $\mu$L of 2,3-dimethyl-1,3-butadiene (6.5 mmol)]. The nitromethane anion was then added [170 $\mu$L of $CH_3NO_2$ (3.1 mmol), 150 mg of NaH (50%, 3.1 mmol), 20 mL of $Me_2SO$, stir 4 h]. The solution formed a yellow precipitate and then turned pea-green to orange to red over 2 min. The reaction was stirred 7 h at room temperature. The standard isolation and purification by Chromatotron (2:1 hexane/ethyl acetate) gave 54 mg (10%, $R_f$ 0.34) of the product as a light yellow oil: $^1H$ NMR ($CDCl_3$) $\delta$ 1.71 (s, 3, $CH_3$), 1.72 (s, 3, $CH_3$), 2.13 (s, 3, $COCH_3$), 2.84 (t, $J$ = 7.5 Hz, 2, $CH_2CH=$), 3.17 (s, 2, $CH_2CO$), 4.43 (t, $J$ = 7.5 Hz, 2, $CH_2NO_2$); IR (neat) 1715 (C=O), 1550 ($CNO_2$) $cm^{-1}$. An analytical sample was obtained by evaporative distillation (56 °C/0.07 mm). Anal. ($C_9H_{15}NO_3$) C, H, N.

In addition, 83 mg (23%, $R_f$ 0.56) of 2,3-dimethyl-1,3-hexadien-5-one[1] was formed: $^1H$ NMR ($CDCl_3$) $\delta$ 1.95 (s, 3, $CH_3$), 2.27 (s, 6, $COCH_3$, $CH_3$), 5.23 (s, 1, $=CHH$), 5.42 (s, 1, $=CHH$), 6.22 (s, 1, $RCH=CR_2$); IR (neat) 1686 (C=O), 1590 (C=C) $cm^{-1}$.

**1-Acetyl-4-(nitromethyl)-1-cyclohexene.** The $\pi$-allyl complex was formed as usual over 6 h [30 mL of 0.54 M $NaCo(CO)_4$ (16.2 mmol), 1.07 mL of $CH_3I$ (17.2 mmol), 100 mL of THF, 3.81 mL of 1,3-cyclohexadiene (40.0 mmol)]. The nitromethane anion was added [1.79 mL of $CH_3NO_2$ (33.0 mmol), 1.584 of NaH (50%, 33.0 mmol), 100 mL of $Me_2SO$, stir 7 h], and the mixture changed from brown-yellow to yellow and then to red. Stirring continued for 17 h at room temperature. The usual isolation and Chromatotron purification (1:1 hexane/ethyl acetate) gave 2.187 g (74%, $R_f$ 0.40) of product: $^1H$ NMR ($CDCl_3$) $\delta$ 2.28 (s, 3, $CH_3CO$), 1.3–2.7 (m, 7), 4.42 (d, $J$ = 6.5 Hz, 2, $CH_2NO_2$), 6.86 (m, 1, =CH); IR ($CHCl_3$) 1665 (C=O), 1550 ($CNO_2$) $cm^{-1}$. Evaporative distillation gave an analytical sample. Anal. ($C_9H_{13}NO_3$) C, H, N.

***cis*-1-Acetyl-4-(nitromethyl)-2,3-dehydrodecalin.** The $\pi$-allyl complex was made over 12 h [(5.00 mL of 0.614 M $NaCo(CO)_4$ (3.07 mmol), 210 $\mu$L of $CH_3I$ (3.3 mmol), 650 $\mu$L of decalin-1,3-diene, 20 mL of THF]. The nitromethane anion [360 $\mu$L of $CH_3NO_2$ (6.6 mmol), 320 mg of NaH (50%, 6.6 mmol), 25 mL of $Me_2SO$, stir 11.5 h] was added, and a yellow-green precipitate formed that dissolved over 10 min. The reaction continued for 8 h. The usual isolation and Chromatotron separation (3:1 hexane/ethyl acetate) gave 392 mg of product (54%, $R_f$ 0.42) as a yellow oil. The obtain an analytical sample, the product was rechromatographed and evaporatively distilled (90 °C/0.005 mm): $^1H$ NMR ($CDCl_3$) $\delta$ 1.0–2.5 (m, 12), 2.18 (s, 3, $COCH_3$), 4.1–4.4 (m, 2, $CH_2NO_2$), 5.1–5.7 (m, 2, olefinic Hs); IR (neat) 1713 (C=O), 1671, 1550 (C-$NO_2$) $cm^{-1}$. Anal. ($C_{13}H_{19}NO_3$) C, H, N.

**4-Acetyl-6-methyldecalin-1,3-diene.** The $\pi$-allyl species was formed over 6 h [4.00 mL of 0.614 M $NaCo(CO)_4$ (2.46 mmol), 165 $\mu$L of $CH_3I$ (2.65 mmol), 930 $\mu$L of 6-methyldecalin-1,3-diene (6.0 mmol), 20 mL of THF]. Nitromethane anion was added [145 $\mu$L of $CH_3NO_2$ (2.65 mmol), 130 mg of NaH (50%, 2.65 mmol), 20 mL of $Me_2SO$, stir 5.5 h], and the solution turned from red-brown to pea-green to yellow to orange to red over 5 min. The mixture was allowed to stir for 13 h at room temperature. The usual isolation and Chromatotron separation (3:1 hexane/ethyl acetate) gave 456 (96%, $R_f$ 0.52) of the dienone, a very light yellow liquid: $^1H$ NMR ($CDCl_3$) $\delta$ 0.86 (s, 3, $CH_3$), 1.2–2.1 (m, 9), 2.31 (s, 3, $COCH_3$), 2.65 (d, $J$ = 16.8 Hz, 1, $CHHC(COCH_3)=$), 5.74 (d, $J$ = 5.7 Hz, 1, CH=C), 6.82 (dd, $J$ = 5.7, 2.9 Hz, 1, CH=CC=O); IR (neat) 1655 (C=O), 1573 ($CNO_2$), 961, 831 $cm^{-1}$.

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Evaporative distillation (with great loss of product) gave an analytical sample (52 °C/0.03 mm). Anal. ($C_{12}H_{18}O$) C, H.

**2-Acetyl-$\Delta^{2,4}$-cholestadiene.** The $\pi$-allyl complex was made over 6.5 h [1.83 mL of 0.589 M $NaCo(CO)_4$ (1.08 mmol), 67 μL of $CH_3I$ (1.08 mmol), 400 mg of $\Delta^{2,4}$-cholestadiene (1.08 mmol), 15 mL of THF]. The nitromethane anion was added [58 μL of $CH_3NO_2$ (1.08 mmol), 52 mg of NaH (50%, 1.08 mmol), 10 mL of $Me_2SO$, stir 6 h], and the mixture was stirred 16.5 h at room temperature. The usual isolation followed by Si gel preparative layer chromatography (developed with hexane three times) gave 206 mg of solid that was purified by Chromatotron (3:1 hexane/ethyl acetate) to give 124 mg (28%) of product: mp 129–130 °C; $^1H$ NMR ($CDCl_3$) δ 0.69 (s, 3, $CH_3$), 0.86 (s, 3, $CH_3$), 0.85 (d, $J$ = 1.4 Hz, 3, $CH(CH_3)CH_3$), 0.87 (d, $J$ = 1.4 Hz, 3, $CH(CH_3)CH_3$), 0.91 (d, $J$ = 6.5 Hz, 3, $CH_3$), 0.91–2.1 (m, 25), 2.31 (s, 3, $COCH_3$), 2.89 (d, $J$ = 16.8 Hz, 1), 5.72 (d, $J$ = 5.7 Hz, 1, =CH), 6.81 (dd, $J$ = 5.7, 2.8 Hz, 1, CH=CC=O); IR (KBr) 1653 (C=O) $cm^{-1}$. Anal. ($C_{29}H_{46}O$) C, H.

**2-(Nitromethyl)-1-[(acetylmethyl)methylene]cyclohexane.** The $\pi$-allyl complex was formed over 6 h [5.00 mL of 0.57 M $NaCo(CO)_4$ (2.85 mmol), 200 μL of $CH_3I$ (3.2 mmol), 15 mL of THF, 800 μL of 1-vinyl-1-cyclohexene (6.2 mmol)], and the nitromethane anion was then added [325 μL of $CH_3NO_2$ (6.0 mmol), 200 mg of NaH (50%, 6.0 mmol), 20 mL of $Me_2SO$, stir 6 h]. The reaction continued for 15.5 h. The usual isolation followed by Chromatotron separation (1:1 hexane/ethyl acetate) gave 123 mg (20%, $R_f$ 0.32) of product: $^1H$ NMR ($CDCl_3$) δ 1.5 (m, 5, $CH_2$), 1.9 (m, 3, $CH_2$), 2.14 (s, 3, $CH_3CO$), ABX system $\delta_A$ 2.57, $\delta_B$ 2.65, $\delta_X$ 5.52 ($J_{AB}$ = 17.2 Hz, $J_{AX}$, $J_{AB}$ = 7.8 Hz, 3, $COCH_2CH$=), 3.23 (q, $J$ = 7 Hz, 1, $CHCH_2NO_2$), 4.40 (m, 2, $CH_2NO_2$); IR ($CHCl_3$) 1718 (C=O), 1550 ($CNO_2$) 1378 $cm^{-1}$. Evaporative distillation gave an analytical sample. Anal. ($C_{11}H_{17}NO_3$) C, H, N.

**1-Nitro-3-methylene-4-pentanone.** The $\pi$-allyl complex was made in the usual manner over 6 h except that the reaction was kept at 0–5 °C [10.00 mL of 0.589 M $NaCo(CO)_4$ (5.89 mmol), 400 μL of $CH_3I$ (6.44 mmol), 30 mL of THF, excess allene]. The nitromethane anion was added at 0 °C [350 μL of $CH_3NO_2$ (6.44 mmol), 309 mg of NaH (50%, 6.44 mmol), 40 mL of $Me_2SO$, stir 6 h] and the reaction continued at ice-bath temperature for 0.5 h. The usual isolation followed by Chromatotron separation (1:1 hexane/ethyl acetate) gave 407 mg (48%, $R_f$ 0.38) of product as a very light yellow liquid: $^1H$ NMR ($CDCl_3$) δ 2.35 (s, 3, $CH_3CO$), 2.94 (t, $J$ = 6 Hz, 2, $=CCH_2$), 4.50 (t, $J$ = 6 Hz, 2, $CH_2NO_2$), 5.97 (s, 1, =CHH), 6.14 (s, 1, =CHH); IR (neat) 1674 (C=O), 1551 ($CNO_2$), 1369 ($CNO_2$) $cm^{-1}$. Evaporation distillation gave an analytical sample (75 °C/0.04 mm). Anal. ($C_6H_9NO_3$) C, H, N.

**1-Nitro-2-methoxy-3-methylene-4-pentanone.** The $\pi$-allyl species was formed as usual and stirred at 0 °C for 4.5 h [5.00 mL of 0.589 M $NaCo(CO)_4$ (2.94 mmol), 200 μL of $CH_3I$ (3.2 mmol), 15 mL of THF, 600 μL of methoxyallene]. The nitromethane anion was added at 0 °C [175 μL of $CH_3NO_2$ (3.2 mmol), 154 mg of NaH (50%, 3.2 mmol), 20 mL of $Me_2SO$, stir 5.5 h] and allowed to react for 0.5 h at 0 °C. The usual isolation with the addition of stirring with 20 mL of 1 N HCl for 1 h, then drying with $MgSO_4$, and separation by Chromatotron (1:1 hexane/ethyl acetate] gave 180 mg (35%, $R_f$ 0.31) of product: $^1H$ NMR ($CDCl_3$) δ 2.38 (s, 3, $COCH_3$), 3.32 (s, 3, $OCH_3$), 4.27 (dd, $J$ = 13 Hz, 8.8 Hz, 1, $CHHNO_2$), 4.55 (dd, $J$ = 13 Hz, 3 Hz, 1, $CHHNO_2$), 4.84 (dd, $J$ = 8.8 Hz, 3 Hz, 1, $CH(OCH_3)$), 6.25 (d, $J$ = 1.5 Hz, 1, C=CHH), 6.35 (s, 1, =CHH); IR ($CHCl_3$) 1677 (C=O), 1559 ($CNO_2$), 1378 ($CNO_2$) $cm^{-1}$. Evaporative distillation gave a light yellow liquid that solidified on standing (82 °C/0.25 mm, mp 44–45 °C). Anal. ($C_7H_{11}NO_4$) C, H, N.

**1-Nitro-3-(bromomethylene)-4-pentanone.** The $\pi$-allyl complex was made over 1.4 h at 0 °C [5.00 mL of 0.614 M $NaCo(CO)_4$ (3.07 mmol), 210 μL of $CH_3I$ (3.3 mmol), 1.00 mL of bromoallene (13.0 mmol), 20 mL of THF]. The nitromethane anion was added [180 μL of $CH_3NO_2$ (3.3 mmol), 160 mg of NaH (50%, 3.3 mmol), 20 mL of $Me_2SO$, stir 5.5 h] at 0 °C, and the immediate evolution of gas followed. Stirring continued 0.5 h. The usual isolation (on addition of saturated ammonium chloride a large amount of brown precipitate formed that was removed) followed by Chromatotron separation (2:1 hexane/ethyl acetate) gave three fractions. The third was rechromatographed (1:1 hexane/$Et_2O$) to give 43 mg (7%, $R_f$ 0.41) of a light yellow oil: $^1H$ NMR ($CDCl_3$) δ 2.37 (s, 3, $CH_3$), 3.19 (t, $J$ = 7.3 Hz, 2, $CH_2CH_2NO_2$), 4.47 (t, $J$ = 7.3 Hz, 2, $CH_2NO_2$), 6.02 (d, $J$ = 4.2 Hz, 1, =CHBr); IR (neat) 1681 (C=O), 1551 ($CNO_2$), 1365 ($CNO_2$) $cm^{-1}$. This material decomposed easily, and an acceptable elemental analysis was not obtained.

**1-Nitro-2-*tert*-butoxy-3-methylene-4-pentanone.** The $\pi$-allyl species was formed over 5 h at 0 °C and then warmed to room temperature for 2.75 h [5.00 mL of 0.614 M $NaCo(CO)_4$ (3.07 mmol), 210 μL of $CH_3I$ (3.3 mmol), 20 mL of THF, 1.5 mL of *tert*-butoxyallene]. The nitromethane anion was added after the solution was cooled to 0 °C [180 μL of $CH_3NO_2$ (3.3 mmol), 160 mg of NaH (50%, 3.3 mmol), 20 mL of $Me_2SO$, stir 5 h]. A yellow precipitate formed and then dissolved over 5 min while stirring continued for 0.5 h at 0 °C. The usual isolation followed by Chromatotron (1:1 hexane/ethyl acetate) separation gave 219 mg of $R_f$ 0.5–0.8 material that was rechromatographed (2:1 hexane/ethyl acetate) to give 50 mg (8%, $R_f$ 0.48) of pure product: $^1H$ NMR ($CDCl_3$) δ 1.13 (s, 9, $CH_3$), 2.40 (s, 3, $COCH_3$), 4.24 (dd, $J$ = 11.4, 8.4 Hz, 1, $CHHNO_2$), 4.43 (dd, $J$ = 11.4, 3.0 Hz, 1, $CHHNO_2$), 5.18 (dd, $J$ = 8.4, 3.0 Hz, 1, CHO-*t*-Bu), 6.34 (s, 1 H, =CHH), 6.42 (s, 1, =CHH); IR (neat) 1675 (C=O), 1556 ($CNO_2$) $cm^{-1}$. Evaporative distillation (70–75 °C/0.01 mm) gave an analytical sample. Anal. Calcd for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51. Found: C, 56.12; H, 7.84; N, 5.68.

**1-(1-Hydroxyethyl)-4-(nitromethyl)cyclohexene.** To 1-acetyl-4-(nitromethyl)cyclohexene (750 mg, 4.09 mmol) in THF (10 mL) under argon at −20 °C was added 1 M DIBAL (diisobutylaluminum hydride) (20 mL, 20 mmol). Stirring continued 2.75 h, and then $CH_3OH$ (30 mL) was added followed by warming to room temperature. The white slurry was stirred 18 h and filtered. The filtrate was concentrated and purified on the Chromatotron (1:3 hexane/ethyl acetate) to give 625 mg (82%, $R_f$ 0.50) of the product as a colorless oil: $^1H$ NMR ($CDCl_3$) δ 1.23 (d, $J$ = 6.5 Hz, 3, $CH_3$), 1.0–2.6 (m, 7), 2.66 (b s, 1, OH), 3.9–4.4 (m, 1, CHOH), 4.30 (d, $J$ = 6Hz, 2, $CH_2NO_2$), 5.6 (b s, 1, =CH); IR ($CHCl_3$) 3460 (OH), 1555 ($CNO_2$), 1386 ($CNO_2$) $cm^{-1}$. Anal. ($C_9H_{15}NO_3$) C, H, N.

**1-(1-Hydroxyethyl)-4-(aminomethyl)cyclohexene.** A solution of 1-(1-hydroxyethyl)-4-(nitromethyl)cyclohexene (273 mg, 1.47 mmol) in $Et_2O$ (20 mL) was added dropwise to a slurry of lithium aluminum hydride (160 mg, 4.45 mmol) in $Et_2O$ (5 mL) at room temperature under argon. The solution was stirred 2 h after addition was complete and then carefully quenched with $H_2O$ (15 mL) and 20% sodium potassium tartrate solution (15 mL). The slurry was stirred 0.5 h, then extracted with $Et_2O$ (4 × 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give 179 mg (78%) of product: $^1H$ NMR ($CDCl_3$) δ 1.15 (d, $J$ = 6 Hz, 3, $CH_3$), 1.4–2.2 (m, 7), 2.50 (d, $J$ = 4.5 Hz, 2, $CH_2NH_2$), 2.86 (s, 2, $NH_2$), 4.05 (q, $J$ = 6 Hz, 1, CHOH), 5.48 (m, 1, =CH); IR (neat) 3000–3700 (br, OH, $NH_2$) $cm^{-1}$.

**3-(4-Acetyl-3-cyclohexenyl)-4,5-dicarbomethoxyisoxazole.** 3-(4-Acetyl-3-cyclohexenyl)-4,5-dicarbomethoxyisoxazole was made following the procedure of Mukaiyama.[15] Triethylamine (250 μL, 1.8 mmol) was added to a solution of 1-acetyl-4-(nitromethyl)-1-cyclohexene (300 mg, 1.64 mmol) in benzene (10 mL). To this solution was added phenyl isocyanate (360 μL, 3.3 mmol) and dimethyl acetylenedicarboxylate (225 μL, 1.8 mmol). The flask was placed under an argon atmosphere and stirred at room temperature for 1 h and then at gentle reflux for 6 h. The solution was cooled, diluted with 30 mL of benzene, and filtered, and the solvent was removed in vacuo to give a red-brown oil that was filtered through a small column of silica gel and purified by Chromatotron (1:2:1 ethyl acetate/hexane/benzene) to give 228 mg of crude product. Kugelrohr distillation (95 °C/0.005 mmHg) gave 195 mg (39%) pure product: $^1H$ NMR ($CDCl_3$) δ 1.8–2.8 (m, 7), 2.30 (s, 3, $COCH_3$), 3.3 (m, 1, CHC=N), 3.88 (s, 3, $COOCH_3$), 3.94 (s, 3, $COOCH_3$), 6.84 (m, 1, =CH); IR (neat) 1740 (C=O) $cm^{-1}$. Evaporative distillation (95 °C/0.005 mm) gave an analytical sample. Anal. ($C_{15}H_{17}NO_6$) C, H, N.

**4-Acetyl-3-cyclohexenecarboxaldehyde.** 4-Acetyl-3-cyclohexenecarboxaldehyde was made by the procedure of McMurray and Melton.[16] A buffered $TiCl_3$ solution was prepared by adding

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$NH_4OAc$ (5.14 g, 66.7 mmol) in $H_2O$ (17 mL) to 20% aqueous $TiCl_3$ (1.715 g, 11.1 mmol, 9 mL of $H_2O$) under argon. This buffered solution was added to a solution of 1-acetyl-4-(nitromethyl)-1-cyclohexene (510 mg, 2.78 mmol), sodium methoxide (150 mg, 2.78 mmol), and methanol (6 mL) and stirred under argon at room temperature for 3.5 h. Dilution with $Et_2O$ (50 mL) and extraction with $Et_2O$ (2 × 50 mL) gave a light yellow organic layer that was washed with saturated $NaHCO_3$ (2 × 50 mL) and brine (1 × 50 mL), dried over $Na_2SO_4$, and filtered, and the solvent was removed in vacuo to give an orange oil. Chromatotron separation (1:1 hexane/ethyl acetate) gave 166 mg (39%) of product. Evaporative distillation (46–48 °C/0.04–0.02 mm) gave an analytical sample: $^1H$ NMR ($CDCl_3$) $\delta$ 1.6–1.8 (m, 2), 2.0–2.2 (m, 1), 2.30 (s, 3, $COCH_3$), 2.35–2.6 (m, 4), 6.92 (m, 1, =CH), 9.73 (s, 1, CHO); IR (neat) 1725 (CHO), 1664 (C=O) $cm^{-1}$. Anal. ($C_9H_{12}O_2$) C, H.

**1-Acetyl-4-(nitromethyl)cyclohexane.** To a Fischer-Porter bottle was added 1-acetyl-4-(nitromethyl)cyclohexane (734 mg, 4.01 mmol), absolute EtOH (20 mL), and $PtO_2$ (45 mg, 0.2 mmol). The bomb was evacuated and filled three times with $H_2$. The third time the bomb was charged with 43 psi of $H_2$, and the contents were stirred 22.5 h at 60 °C. The contents of the reactor were cooled, diluted with $Et_2O$ (50 mL), gravity filtered, dried with $MgSO_4$, filtered again, and concentrated in vacuo. The yellow oil was purified by Chromatotron (1:3 hexane/ethyl acetate) to give 370 mg (50%, $R_f$ 0.53) of product as a colorless oil: $^1H$ NMR ($CDCl_3$) $\delta$ 1.38 (m, 2), 1.65 (m, 4), 1.96 (m, 2), 2.16 (s, 3, $COCH_3$), 2.32 (m, 1), 2.57 (quint, $J$ = 5.1 Hz, 1, CHCO), 4.28 (d, $J$ = 7.4 Hz, 2, $CH_2NO_2$); IR (neat) 1710 (C=O), 1550 ($CNO_2$) $cm^{-1}$. An analytical sample was obtained by evaporative distillation (62 °C/0.025 mm). Anal. ($C_9H_{15}NO_3$) C, H, N.

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**Registry No.** 1, 33482-84-7; 2, 4117-50-4; *trans*-$CH_3C(O)CH_2CH{=}CH(CH_2)2NO_2$, 90295-76-4; *trans,trans*-$(CH_3C(O)CH_2CH{=}CHCH_2)_2CHNO_2$, 90341-46-1; *trans*-$CH_3C(O)CH_2CH{=}CHCH_2CH(NO_2)CH_3$, 90295-77-5; *trans,trans*-$(CH_3C(O)CH_2CH{=}CHCH_2)_2C(NO_2)CH_3$, 90295-78-6; *trans*-$CH_3C(O)CH_2CH{=}CHCH_2C(CH_3)_2NO_2$, 90295-79-7; *trans*-$CH_3C(O)CH_2C(CH_3){=}C(CH_3)_2NO_2$, 90295-80-0; $CH_3C(O)C(=CH_2)(CH_2)_2NO_2$, 90295-84-4; $CH_3C(O)C(=CH_2)CH(OMe)CH_2NO_2$, 90295-85-5; $CH_3C(O)C(=CH_2)CH(t\text{-}BuO)CH_2NO_2$, 90295-86-6; $CH_3C(O)C(=CHBr)(CH_2)_2NO_2$, 90295-87-7; $CH_2{=}CHCH{=}CH_2$, 106-99-0; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}C{=}CH_2$, 463-49-0; $CH_2{=}C{=}CHOCH_3$, 13169-00-1; *t*-$BuOCH{=}C{=}CH_2$, 33721-28-7; $CH_2{=}C{=}CHBr$, 10024-18-7; $CH_2NO_2^-$, 18137-96-7; $CH_3CHNO_2^-$, 25590-58-3; $(CH_3)_2CNO_2^-$, 20846-00-8; $NaCo(CO)_4$, 14878-28-5; $Co_2(CO)_8$, 10210-68-1; MeI, 74-88-4; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; 1-acetyl-4-(nitromethyl)-1-cyclohexene, 90295-81-1; *cis*-1-acetyl-4-(nitromethyl)-2,3-dehydrodecalin, 90295-82-2; 2-(nitromethyl)-1-[(acetylmethyl)methylene]cyclohexane, 90295-83-3; 1,3-cyclohexadiene, 592-57-4; 1,2,3,4,4a,8a-hexahydronaphthalene, 62690-62-4; 1-vinyl-1-cyclohexene, 2622-21-1; 1-acetyl-6-methyldecalin-1,3-diene, 90295-88-8; 6-methyldecalin-1,3-diene, 90295-89-9; 2-acetyl-$\Delta^{2,4}$-cholestadiene, 90341-54-1; $\Delta^{2,4}$-cholestadiene, 4117-50-4; 1-(1-hydroxyethyl)-4-(nitromethyl)cyclohexene, 90295-90-2; 1-(1-hydroxyethyl)-4-(aminomethyl)cyclohexene, 90295-91-3; 3-(4-acetyl-3-cyclohexyl)-4,5-dicarbomethoxyisoxazole, 90295-92-4; 4-acetyl-3-cyclohexenecarboxaldehyde, 90295-93-5; 1-acetyl-4-(nitromethyl)cyclohexane, 90295-94-6.

# Relative Reactivities of Alkylbenzenes and Related Compounds toward Ozone. The Mechanism of Ozonation at Benzylic Positions

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Four monoalkylbenzenes and selected polyphenylalkanes, fluorenes, and partially reduced anthracenes and phenanthrenes were ozonized at 25 °C in dichloromethane, and relative reactivities were determined. These reactivities can be divided into the percent of ring ozonation plus the percent of reaction at the benzylic position (which yields hydrotrioxides) by comparison with related systems that undergo only the former reaction. (For example, the relative reactivities of toluene and *tert*-butylbenzene can be compared to determine the relative reactivity of toluene's benzylic position.) Introduction of either one or two methyl or phenyl groups at the exocyclic position of toluene markedly increases benzylic reactivity. Although 9,10-dihydroanthracene derivatives are structurally similar to diphenylmethane, their benzylic reactivity toward ozone is some 50 times greater on a per hydrogen basis; this is explicable in terms of the greater ease of achieving a planar transition state in the former case and the resultant greater delocalization in the benzylic intermediate. The relatively modest amount of benzylic reaction for fluorene leads us to propose that the intermediate involved in hydrotrioxide formation is a carbocationic species, rather than a free radical, in agreement with the recent suggestion of Nangia and Benson.

We recently reported a study of the ozonation of cumene in which the total reactivity was separated into ring ozonation and attack on the side-chain benzylic hydrogen.[2,3] Attack at the benzylic position produces cumyl hydrotrioxide, $PhCMe_2OOOH$, which decomposes above about −20 °C to produce free radicals. In an effort to understand the factors that affect the production of hydrotrioxides in the ozonation of aralkyl compounds, we here report a study of the ozonation of four monoalkyl benzenes and several related compounds.

The ozonation of alkyl- and polyalkylbenzenes has been reported by several groups.[4-6] The most extensive study

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