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1,2- and 1,4-Addition in the Reactions of Carbonyl Compounds with 1,3-Butadiene Induced by Cerium(IV) Ammonium Nitrate

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CAN-promoted oxidative additions of acetone, 2-butanone, 3-methyl-2-butanone, and ethyl acetoacetate to 1,3-butadiene have been investigated. In all cases the major primary reaction products are 1,2- and 1,4-adducts, 4-(β-ketoalkyl)-substituted 3-nitrate-1-butene and 1-nitrate-2-butene, respectively, which form in an overall yield between 70 and 97%. With unsymmetrical ketones the reaction exclusively involves the more substituted α-carbon (2-butanone), and attack from the isopropyl side significantly competes with the one from the methyl side (3-methyl-2-butanone). The ratio between 1,2- and 1,4-adducts is not far from unity and does not significantly depend on the carbonyl compound structure. 1,4-Adducts are easily isolated whereas 1,2-adducts are unstable and decompose to complex mixtures when formed from ketones and to a dihydrofuran derivative when formed from ethyl acetoacetate. Since oxidative addition is faster than the reaction of CAN with the carbonyl compound, a mechanism is suggested involving attack on the diene of a cerium-coordinated ketoalkyl free radical in equilibrium with a cerium(IV)-carbonyl complex.

Oxidative addition of enolizable carbonyl compounds to alkenes promoted by one-electron oxidants is a well-known reaction which has received considerable attention in recent years.[1-9] Even if this reaction has not been thoroughly investigated from the mechanistic point of view the process is most frequently formulated as shown in Scheme I (where, for example, the oxidant is a metal ion M^{n+} and X^- is a basic species present in the medium or one of the ligands of the metal).

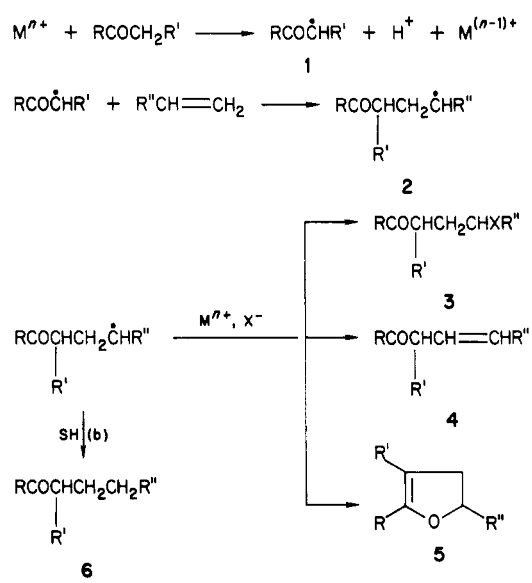
The carbonyl compound is first oxidized to give the electrophilic α-ketoalkyl radical 1 capable of adding to the alkene before undergoing further oxidation. The new radical formed (2), now a nucleophilic species, can then be easily oxidized (path a) by M^{n+} to give the products 3-5. In Scheme I a *nonoxidative* route available to the radical 2 is also indicated: a hydrogen atom abstraction process leading to 6 (path b). In this case if SH is the carbonyl compound itself, a chain reaction can take place. So far, most of the work in this area has concerned the use of $Mn(OAc)_3$ as the oxidizing species. With this oxidant, in AcOH, reaction of simple ketones leads to a mixture of products 3, 4, and 6.[1] Much better results, from the synthetic point of view, have been obtained with β-keto esters and β-diketones. In this case predominant formation of dihydrofurans (5) can be observed expecially with alkenylaromatics[3a] and conjugated dienes as olefinic substrates.[3a,9] Substantially similar results are obtained with Pb(IV) and Ag(II) oxides,[5] but a different situation arises with $S_2O_8^{-2}/Ag^+$ which, with ketones and β-diketones produces good yields of the addition product 6 in a chain reaction.[4] Some important synthetic applications of this type of reaction have recently been reported.[10]

It is generally stated that Ce(IV) salts and $Mn(OAc)_3$ give similar results;[1,2] however information on the reactions promoted by Ce(IV) is very scanty. Since our previous work on the reactions of ceric ammonium nitrate (CAN) with alkyl and alkenyl aromatic compounds has clearly shown that this oxidant can often exhibit quite peculiar properties as compared to other metal ions,[11] we have considered it worthwhile to undertake a detailed investigation of the CAN-promoted oxidative addition of enolizable carbonyl compounds to alkenes.

In this paper we report on the addition of acetone, 2-butanone, 3-methyl-2-butanone, and ethyl acetoacetate to 1,3-butadiene. Since CAN is very efficient in promoting oxidation of radicals by a ligand transfer mechanism,[12] we hoped to have predominant formation of type 3 products ($X = ONO_2$), in the specific case of allyl nitrates, which might be useful synthetic intermediates due to the possibility of replacement or conversion of the nitrate group.

Moreover, it was considered useful to acquire information on the competition between 1,2- and 1,4-addition and on the chemoselectivity of the process when unsymmetrical

Scheme I



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ketones are involved. This information, which is also of interest from the synthetic point of view, should allow a more detailed comparison between CAN and $Mn(OAc)_3$ behavior.

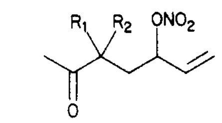
Results

Acetone, 2-butanone, and 3-methyl-2-butanone were made to react with CAN and 1,3-butadiene, the solvent being the reactant ketone in each case. The CAN:1,3-butadiene molar ratio was 1:2. Solvents different than the reactant ketones were also used but with worse results. Accordingly, in CH_3CN reactions were exceedingly slow, and in MeOH extensive solvolysis of the reaction products was observed.

Reactions of ethyl acetoacetate were much faster than those of simple ketones and were therefore conveniently carried out either in acetonitrile or MeOH with a 1:2:2 ester:CAN:butadiene molar ratio.

In all cases usual workup of the reaction mixture gave a crude product whose spectroscopic properties were satisfactorily accounted for by a mixture of 4-(β-ketoalkyl)-substituted 3-nitrate-butene-1 and 1-nitrate-butene-2, 1,2- and 1,4-addition products, respectively. On the basis of ^1H NMR coupling constants and IR spectra the 1,4-adducts were assigned a trans structure, which is in line with previous observations concerning free radical additions to conjugate dienes.[13]

Thus, the reaction of acetone, CAN, and 1,3-butadiene leads to a mixture of **7a** and **8a** whereas **7b** (a mixture of diastereoisomers) and **8b** are formed in the corresponding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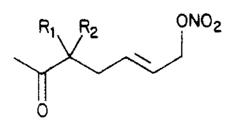
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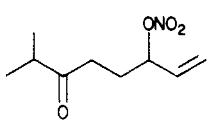
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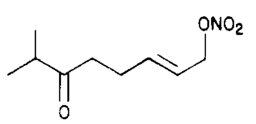
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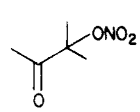
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a, $R_1 = R_2 = H$; **b**, $R_1 = H$, $R_2 = CH_3$; **c**, $R_1 = R_2 = CH_3$; **d**, $R_1 = H$, $R_2 = CO_2C_2H_5$

reaction of 2-butanone. Interestingly, reaction of this ketone involves the substituted α-carbon atom exclusively. In the reaction of 3-methyl-2-butanone both α-carbon atoms of the ketone take part in the addition, and adducts **9** and **10** are formed together with **8c**. Another product of this reaction is the nitrate **11**, i.e., the product of direct oxidation of 3-methyl-2-butanone.

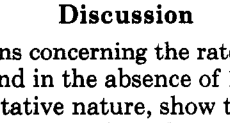
When the carbonyl compound is ethyl acetoacetate, the reaction leads to **7d** and **8d** in CH_3CN, the reacting carbon being exclusively that α to both carbonyl groups. It is noteworthy that **7d** and **8d** are the major products also when the reaction is run in MeOH.

The yields of 1,2 and 1,4-adduct in the various reactions were determined in the crude product by ^1H NMR analysis (thermal decomposition of nitrates precluded the use of GLC), with p-dimethoxybenzene as internal standard (Table I). Determinations at different percents of reaction indicated that there is no interconversion between the 1,2 and 1,4-adducts.

The data reported in Table I show that in the reactions of acetone and 2-butanone the material balance is not very good, 1,2- and 1,4-adducts accounting for about 70% of reacted CAN. For the major part this is very probably due to a competing direct reaction between CAN and ketones leading to low molecular weight and water soluble oxidation products.[14] In agreement with this hypothesis the material balance is nearly 100% in the reaction of 3-methyl-2-butanone where the ketone oxidation product **11** was detected in 17% yield.

An important observation is also that the rate of CAN reduction in the various ketones is ca. 3–4 times slower than the one observed under the same conditions but in the presence of 1,3-butadiene. Thus there must be competition between oxidation of ketone and oxidative addition to 1,3-butadiene. With ethyl acetoacetate the rate of oxidation of the keto ester by CAN is negligible with respect to that of the oxidative addition to the diene and accordingly nitrates **7d** and **8d** account for nearly 100% of reacted CAN. Other interesting implications of these observations will be discussed later.

The 1,4-adducts were easily isolated by column chromatography (silica gel) of the crude product in yields that were in excellent agreement with those determined by ^1H NMR analysis. On the contrary, 1,2-adducts obtained in the ketone reactions were unstable under the chromatography conditions and underwent considerable decomposition to a complex mixture of products, which was not further elaborated.[15] The 1,2-adduct **7d** formed in the reaction of ethyl acetoacetate was also unstable; however, in this case decomposition led to the cyclization product **12**. The yield of isolated **12** was almost identical with that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of **7d** determined in the crude product. For these reasons 1,2-adducts were isolated (in some cases after purification by preparative HPLC) in much smaller amounts than the ones originally present in the reaction mixture.

Table I. Reaction Products of the Oxidative Addition of Carbonyl Compounds to 1,3-Butadiene Promoted by CAN at Room Temperature

carbonyl compound	reaction time, h	products (%)[a] 1,2-adduct	1,4-adduct
acetone[b]	24	**7a** (30)	**8a** (38)
2-butanone[b]	5	**7b** (31)	**8b** (38)
3-methyl-2-butanone[b,c]	8	**9** (31)	**10** (36); **8c** (13)
ethyl acetoacetate[d]	0.1	**7d** (52)	**8d** (45)

[a] calculated from ^1H NMR spectrum (see Experimental Section). [b] Ketone as solvent; CAN, 18 mmol; 1,3-butadiene, 36 mmol. [c] In this case also 2-methyl-3-oxobutan-2-ol nitrate (11) (17%) was observed. [d] Solvent CH_3CN (100 mL); CAN, 18 mmol; 1,3-butadiene, 18 mmol; ethyl acetoacetate, 9 mmol.

Discussion

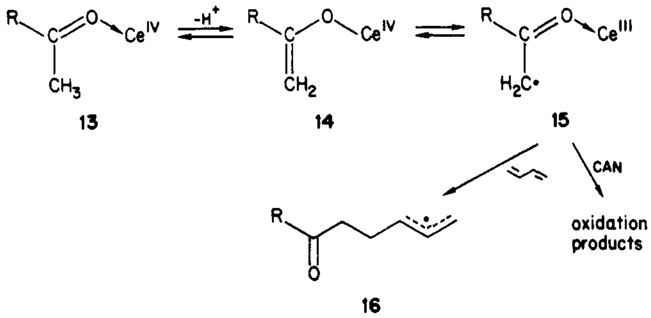
The observations concerning the rate of CAN reduction in the presence and in the absence of 1,3-butadiene, even though of a qualitative nature, show that the rate of oxidative addition is faster than the oxidation reaction of carbonyl compound by CAN, the rate difference being particularly large in the case of ethyl acetoacetate. This finding has a bearing with respect to the reaction mechanism since it is inconsistent with the irreversible formation

(13) See for example: Oswald, A. A.; Griesbaum, K.; Thalen, W. A.; Hudson, B. E., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 3897–3904.

(14) Shorter, J. *J. Chem. Soc.* **1950**, 3425–3431.

(15) It was noted that isolated 1,2-adducts (see text) become rapidly dark freeing HNO_3. Thus, the low stability of these adducts as compared to 1,4-adducts is probably due to the fact that the former can lose HNO_3 presumably giving acid-sensitive dienic species.

Scheme II



of the α-keto radical 1 suggested in Scheme I, such a hypothesis requiring that the rate of CAN reduction by the carbonyl compounds is unaffected by the added diene.

It is worth noting that similar results have been reported for corresponding processes involving $Mn(OAc)_3$, conjugated dienes and β-diketo compounds.[9] In that case too the intermediacy of α-keto radicals was excluded and it was suggested that carbonyl compound and diene react with one another, being both coordinated to Mn(III).

It is doubtful that the hypothesis proposed for the reactions of $Mn(OAc)_3$ also holds for Ce(IV)-induced additions in view of the little or no tendency of lanthanides to form coordination complexes with π-bonding ligands.[16] A tentative suggestion, compatible with the rate effects discussed above, is that the diene attacking species is a cerium(III)-coordinated free radical (**15**) which is in equilibrium with the CAN–carbonyl complex **13**, possibly through the intermediacy of the species **14**. As indicated in Scheme II, **15** can either react with the diene to give the allyl radical **16** or undergo further reaction with CAN to form the carbonyl compound oxidation product. If the latter reaction is slower than the former, the observed effects of added 1,3-butadiene on the reduction rate of CAN by enolizable carbonyl compounds are accounted for.

Complexes of Ce^{IV} with oxygen compounds are well known,[16,17] and more significantly it has been shown that a complex between CAN and acetone is the intermediate in the oxidation of this ketone by ceric salts.[18] The mechanism reported in Scheme II might hold for the corresponding $Mn(OAc)_3$-promoted reactions as well and interestingly equilibria somewhat similar to the ones reported in Scheme II have also been proposed for this oxidant.[19]

The allyl radical **16** once formed reacts with CAN to give the 1,2- and 1,4-addition products. The great ability of CAN to react by an oxidative pathway is indicated by the observation that under our conditions competition by the hydrogen atom transfer reaction (path b in Scheme I) is not significant even when ketones, which are good hydrogen atom donors and are present in great excess, are involved.

The oxidation of the allyl radicals by CAN is probably a ligand-transfer process,[11] this suggestion being also supported by the finding that in the reaction of CAN with ethyl acetoacetate and 1,3-butadiene in MeOH no significant incorporation of the nucleophilic solvent in the reaction product is observed.

Data in Table I also show that there is a slight preference for 1,4-addition in the reactions of acetone, 2-butanone, and 3-methyl-2-butanone (attack from the methyl side), whereas practically equal amounts of the two adducts are obtained in the reaction of ethyl acetoacetate. Exclusive 1,4-addition is, however, observed with 3-methyl-2-butanone for the process involving the dimethyl-substituted α-carbon, this result being most probably due to steric effects which disfavour the formation of the 1,2-adduct.

According to the Kochi's studies on the copper(II)-catalyzed peroxides additions to 1,3-butadiene,[20] a ligand transfer process should lead to predominant formation of the 1,4-addition product. However, in our system a more complicated situation might arise due to the very plausible hypothesis that coordination of CAN with the carbonyl group of the ketoallyl radical precedes the ligand transfer step. Such a coordination might favor the formation of the 1,2-adduct for geometrical reasons and thus justify the fact that the expectation of predominant 1,4-addition is fulfilled only to a small extent or not at all.

Interestingly, in the reaction of $Mn(OAc)_3$ with ethyl acetoacetate and 1,3-butadiene, catalyzed by copper(II) salts, there is no evidence for the formation of addition products.[9] Only **12** is formed, which is described as a primary oxidation product of the allyl radical. In our CAN-promoted reactions, **12** forms from **7d**, presumably via a nitrate displacement reaction induced by the neighboring carbonyl group.

These different behaviors are probably related to substantial differences in the nature of the oxidation step of the allyl radical by the two oxidizing systems. With CAN a ligand-transfer process takes place whereas with $Mn(OAc)_3/Cu(II)$ the alyl radical is oxidized, presumably by copper(II), in a process possessing predominant electron transfer character. An allyl carbocation is then formed, which undergoes rapid cyclization to the dihydrofuran derivative before being attacked by an external nucleophile.[21]

Regarding the chemoselectivity of the process with unsymmetrical ketones results in Table I indicate that with 2-butanone attack of the more substituted α-carbon of the ketone is highly favored since only **7b** and **8b** are formed. After correction for the statistical factor a slight preference for attack of the dimethyl-substituted α-carbon is also observed in the 1,4-addition of 3-methyl-2-butanone (compare yields of **8c** and **10**).

These findings are consistent with previous mechanistic suggestions since predominant formation of the complexes species involving the more stable free radical is expected. Very remarkably this factor can overcome (2-butanone) or counterbalance (3-methyl-2-butanone) both polar (methyl substitution decreases the electrophilic properties of the radical) and steric effects which should favor attack of the less substituted α-carbon.

Another observation is that CAN behaves differently than $Mn(OAc)_3$ also with respect to chemoselectivity. Accordingly, in the reaction of 2-octanone with propenyl acetate induced by $Mn(OAc)_3$ the major addition product is that involving the unsubstituted α-carbon.[3b]

Finally, it should be briefly commented the finding that formation of cyclization products from 1,2-adduct is observed only in the reaction of ethyl acetoacetate. Probably

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(17) Mendelsohn, M.; Arnett, E. M.; Freiser, H. *J. Phys. Chem.* **1960**, *64*, 660–664.

(18) Venkatakrishnan, S.; Santappa, M. *Z. Phys. Chem. (Munich)* **1958**, *16*, 73–84.

(19) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, Chapter 11, p 656.

(20) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 2785–2793.

(21) In agreement with this observation CAN and $Mn(OAc)_3$ behave similarly in the acetonylation of aromatics.[22] Probably in this case both oxidants react with the first formed cyclohexadienyl radical by an electron-transfer mechanism.

(22) Kurz, M. E.; Baru, V.; Nguyen, P. Nhi *J. Org. Chem.* **1984**, *49*, 1603–1607.

7d undergoes cyclization more easily than the other 1,2-adducts since only in the former case the cyclic carbocation, presumably first formed by attack of the carbonyl group to the nitrate bearing carbon, can lose a proton to give a carbonyl conjugated duble bond.

Experimental Section

^{1}H NMR spectra at 90 MHz were registered with a Varian EM 390 spectrometer for solutions in CCl_4. ^{1}H NMR spectra at 400 MHz were registered with a Bruker BR30/60K spectrometer for solutions in $CDCl_3$. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Mass spectra were measured on a MAT 311 A spectrometer. Elemental analyses were performed on a Carlo Erba Elemental Analyser Mod. 1106. Reagents (ERBA RPE) were used as received from the commercial source.

Oxidative Addition of Ketones to 1,3-Butadiene. To a suspension of CAN (10.0 g, 18 mmol) in 100 mL of ketone, butadiene (3 mL, 36 mmol) was added at room temperature. The mixture was allowed to react, while stirring, until complete disappearance of CAN by iodometric titration (5, 10, and 24 h for 2-butanone, 3-methyl-2-butanone, and acetone, respectively). The mixture was poured into cold water and extracted with four 100-mL portions of ether. The combined organic extracts were dried ($CaSO_4$) and concentrated at reduced pressure to yield a yellow oil. *In the reaction with acetone* chromatography of the crude reaction product on silica gel (elution with light petroleum-diethyl ether 8:2) afforded first a very complex mixture of products followed by some fractions containing a compound which after further purification by HPLC (μ-porasil TL column, chloroform as the eluent) was identified as the 1,2 addition product **7a** on the basis of elemental and spectral analysis: ^{1}H NMR analysis of the complex mixture of products obtained in the first fraction showed that none of these compounds were present in the crude reaction product and blank experiments showed that they derive for the most part from decomposition of the 1,2-adduct. No attempt to further elaborate this mixture was therefore carried out.

The last fraction of the chromatography contained a compound which was identified as 6-oxo-2(E)-hepten-1-ol nitrate (**8a**) on the basis of elemental and spectral analysis. The yields of isolated product was 530 mg (34%). The structure of the reaction products were assigned on the basis of the following spectral and elemental analysis results.

6-Oxo-1-hepten-3-ol nitrate (7a): ^{1}H NMR (90 MHz, CCl_4) δ 5.99–5.59 (m, 1 H, H_2), 5.47–5.17 (m, 3 H, H_1 and H_3), 2.51 (t, J = 7 Hz, 2 H, H_5), 2.11 (s, 3 H, H_7), 1.95 (br q, J = 7 Hz, 2 H, H_4); IR (neat) 3090, 2960–2880, 1720, 1630, 1280, 1420, 990 cm^{-1}; MS (45 eV), m/z (relative intensity) 127 (M^+–NO_2) (10), 111 (7), 83 (6), 67 (7), 43 (100). Anal. Calcd for $C_7H_{11}NO_4$: C, 48.55; H, 6.40; N, 8.09. Found: C, 48.45, H, 6.22; N, 8.03.

6-Oxo-2(E)-hepten-1-ol nitrate (8a): ^{1}H NMR (90 MHz, CCl_4) δ 5.86 (dt, J = 15 and 6 Hz, 1 H, H_2), 5.57 (dt, J = 15 and 6 Hz, 1 H, H_3), 4.81 (d, J = 6 Hz, 2 H, H_1), 2.60–2.20 (m, 4 H, H_4 and H_5), 2.09 (s, 3 H, H_7); IR (neat) 3005, 2960–2880, 1720, 1630, 1280, 975 cm^{-1}; MS (45 eV), m/z (relative intensity) 127(M^+ – NO_2) (10), 111 (8), 67 (7), 43 (100). Anal. Calcd for $C_7H_{11}NO_4$: C, 48.55; H, 6.40; N, 8.09. Found: C, 47.92; H, 6.58; N, 8.01. The same procedure described above was used to isolate and characterize the products from 2-butanone and 3-methyl-2-butanone. The structure of reaction products and, where available, the yields are as follows.

From 2-Butanone. 5-Methyl-6-oxo-1-hepten-3-ol nitrate (7b): ^{1}H NMR (90 MHz, CCl_4) δ 5.97–5.60 (m, 1 H, H_2), 5.49–5.10 (m, 3 H, H_1 and H_3), 2.85–1.42 (m, 3 H, H_4 and H_5), 2.13 (s, 3 H, H_7), 1.17 (d, J = 7 Hz, 3 H, 5-CH_3); IR (neat) 3095, 2980, 2880, 1715, 1630, 1280, 990 cm^{-1}; MS (45 eV), m/z (relative intensity) 141 (M^+ – NO_2) (3), 140 (23), 124 (14), 94 (32), 82 (83), 43 (100). NMR spectrum at 400 MHz showed that **7b** is a mixture of diastereoisomers in practically equal amounts. **5-Methyl-6-oxo-2(E)-hepten-1-ol nitrate (8b)** (590 mg, 34% of isolated product): ^{1}H NMR (90 MHz, CCl_4) δ 5.81 (dt, J = 15 and 6 Hz, 1 H, H_2), 5.58 (dt, J = 15 and 6 Hz, 1 H, H_3), 4.82 (d, J = 6Hz, 2 H, H_1), 2.67–2.16 (m, 3 H, H_4 and H_5), 2.08 (s, 3 H, H_7), 1.10 (d, J = 7 Hz, 3 H, 5-CH_3); IR (neat) 2970– 2880, 1710, 1630, 1280, 970 cm^{-1}; MS (45 eV) m/z (relative intensity) 141 (M^+ – NO_2) (13), 126 (10), 81 (32), 43 (100). Anal. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 50.93; H, 7.09; N, 7.60.

From 3-Methyl-2-butanone. 5,5-Dimethyl-6-oxo-2(E)-hepten-1-ol nitrate (8c) (180 mg, 10% of isolated product): ^{1}H NMR (90 MHz, CCl_4) δ 5.78 (dt, J = 15 and 6 Hz, 1 H, H_2), 5.56 (dt, J = 15 and 6 Hz, 1 H, H_3), 4.82 (d, J = 6 Hz, 2 H, H_1), 2.26 (d, J = 6Hz, 2 H, H_4), 2.07 (s, 3 H, H_7), 1.11 (s, 6 H, *gem*-CH_3); IR (neat) 2980–2860, 1710, 1630, 1280, 975, 860 cm^{-1}; MS (45 eV), m/z (relative intensity) 155 (M^+ – NO_2) (38), 139 (20), 95 (40), 81 (26), 55 (27), 43 (100). Anal. Calcd for $C_9H_{15}NO_4$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.20; H, 7.49; N, 6.52. **7-Methyl-6-oxo-1-octen-3-ol nitrate (9)**: ^{1}H NMR (90 MHz, CCl_4) δ 5.97–5.60 (m, 1 H, H_2), 5.47–5.17 (m, 3 H, H_1 and H_3), 2.77–2.29 (m, 3 H, H_5 and H_7), 1.96 (br q, J = 6 Hz, 2 H, H_4), 1.08 (d, J = 7 Hz, 6 H, H_8 and 7-CH_3). **7-Methyl-6-oxo-2(E)-octen-1-ol nitrate (10)**: ^{1}H NMR (90 MHz, CCl_4) δ 5.89 (dt, J = 15 and 6 Hz, 1 H, H_2), 5.56 (dt, J = 15 and 6 Hz, 1 H, H_3), 4.80 (d, J = 6 Hz, 2 H, H_1), 2.67–2.24 (m, 5 H, H_4, H_5, and H_7), 1.08 (d, J = 7 Hz, 6 H, H_8 and 7-CH_3); **9** and **10** were contamined by **11** (10%) so they were not characterized further. Their structures were assigned on the basis of NMR spectra nearly identical with the ones of **7a** and **8a**, respectively, except for the presence of the doublet at δ 1.08 and the absence of the singlet at δ 2.1.

2-Methyl-3-oxobutan-2-ol nitrate (11): ^{1}H NMR (90 MHz, CCl_4) δ 2.18 (s, 3 H, CH_3CO–), 1.54 (s, 6 H, $(CH_3)_2C(ONO_2)$–); IR (neat) 3000–2920, 1735, 1630, 1300, 1120, 850 cm^{-1}. Anal. Calcd for $C_5H_9NO_4$: C, 40.82; H, 6.17; N, 9.52. Found: C, 40.78; H, 6.18, N, 9.32.

Oxidative Addition of Ethyl Acetoacetate to Butadiene. To a solution of CAN (10.0 g, 18.0 mmol) and butadiene (1.5 mL, 18 mmol) in acetonitrile (100 mL), ethyl acetoacetate (1.2 g, 9.2 mmol) was added at room temperature while stirring. The mixture was allowed to react until a colorless solution and a white precipitate were observed (5 min). After the usual workup, the ^{1}H-NMR spectrum of the crude product showed a doublet at δ 4.83 characteristic of the 1,4-nitrate adducts, a multiplet at δ 5.5–4.9 characteristic of the 1,2-nitrate adducts other than two partially superimposed triplets at δ 3.62–3.32 and two singlets at δ 2.21 and 2.18. Chromatography on silica gel, after elution with light petroleum-ethyl ether (8:2), afforded g 0.76 (46%) of a compound which was shown to be the dihydrofuran **12** by comparing its spectral properties with those of literature.[23] The narrow triplet at δ 2.15 (J = 15 Hz, 2-CH_3) and the multiplet at δ 3.19–2.47 (cyclic methylene) of **12** were not present in the ^{1}H NMR spectrum of the crude reaction product. By further elution a small amount (55 mg) of a product was obtained, which was assigned the structure of 1,2-addition product, **5-carbethoxy-6-oxo-1-hepten-3-ol nitrate (7d)**: ^{1}H NMR (90 MHz, CCl_4) δ 6.00–5.63 (m, 1 H, H_2), 5.47–5.12 (m, 3 H, H_1 and H_3), 4.20 (q, J = 7 Hz, 2 H, –$COOCH_2CH_3$), 3.53 (t, J = 7 Hz, 1 H, H_5), 2.21 (s, 3 H, H_7), 2.20–2.00 (m, 2 H, H_4), 1.30 (t, J = 7 Hz, 3 H, –$COOCH_2CH_3$); An attempt to further purify **7d** for the elemental analysis was unsuccessful since **7d** converted into **12** under the chromatography conditions.

The last chromatography fractions contained 960 mg (43%) of a product which was attributed the structure of the 1,4-adduct, **5-carbethoxy-6-oxo-2(E)-hepten-1-ol nitrate (8d)**, on the basis of the following characteristics: ^{1}H NMR (90 MHz, CCl_4) δ 5.84 (dt, J = 15 and 6 Hz, 1 H, H_2), 5.59 (dt, J = 15 and 6 Hz, 1 H, H_3), 4.83 (d, J = 6 Hz, 2 H, H_1), 4.17 (q, J = 7 Hz, 2 H, –$COOCH_2CH_3$), 3.44 (t, J = 6 Hz, 1 H, H_5), 2.56 (br t, J = 6 Hz, 2 H, H_4), 2.18 (s, 3 H, H_7), 1.28 (t, J = 7 Hz, 3 H, –$COOCH_2CH_3$); IR (neat) 2980–2880, 1740, 1720, 1630, 1280, 975 cm^{-1}; MS (70 eV), m/z (relative intensity) 245 (M^+) (1), 199 (M^+–NO_2) (8), 183 (8), 43 (100). Anal. Calcd for $C_{10}H_{15}NO_6$: C, 48.98; H, 6.16; N, 5.71. Found: C, 48.38; H, 6.09; N, 5.40.

The same products were obtained when the reaction was carried out in MeOH.

Yields of the 1,2- and 1,4-Addition Products. Owing to the easy decomposition of the 1,2-adducts under the separation conditions, the yields of 1,2- and 1,4-adducts were determined in the crude mixture by ^{1}H NMR analysis at 400 MHz, except for the reaction products of ethyl acetoacetate for which measures

(23) Bahurel, Y.; Collonges, F.; Manet, A.; Pautet, F.; Poncet, A.; Descotes, G. *Bull. Soc. Chim. Fr.* **1971**, 2203–2208.

at 90 MHz were satisfactory. In all cases *p*-dimethoxybenzene was the internal standard. The quartets at δ 1.942 and 2.317 due to the H_4 protons were used for **7a** and **8a** respectively. Doublets at δ 1.150 and at δ 1.087 due to the 5-CH_3 group were used for **7b** and **8b** respectively. Quartets at δ 2.330 and at δ 1.966 (H_4 protons) and singlets at δ 2.188 and 2.100 (CH_3CO–) were used for **10**, **9**, **11**, and **8c**, respectively. The multiplet at δ 5.49–5.10 (H_1 and H_3) and the triplet at δ 2.56 (H_4 protons) were used for **7d** and **8d**, respectively.

Rate of Reaction of CAN with Carbonyl Compounds. The rate of disappearance of CAN in solutions containing the various carbonyl compounds were determined by iodometric analysis in the absence and in the presence of 1,3-butadiene. With acetone, the half-life time of CAN was 5 h in the presence and 17 h in the absence of 1,3-butadiene. Corresponding values for 2-butanone were 0.75 and 2.3 h. With ethyl acetoacetate the disappearance of CAN was almost instantaneous in the presence of 1,3-butadiene, whereas in the absence of diene only 58% of CAN was reduced after 30 min. With 3-methyl-2-butanone reduction of CAN was complete after 8 and 24 h, in the presence and in the absence of 1,3-butadiene, respectively.

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Registry No. **7a**, 100431-93-4; **7b** (isomer 1), 100431-95-6; **7b** (isomer 2), 100431-96-7; **7d**, 100432-01-7; **8a**, 100431-94-5; **8b**, 100431-92-3; **8c**, 100431-97-8; **8d**, 100432-02-8; **9**, 100431-98-9; **10**, 100431-99-0; **11**, 100432-00-6; **12**, 33626-83-4; CAN, 16774-21-3; acetone, 67-64-1; 2-butanone, 78-93-3; 3-methyl-2-butanone, 563-80-4; ethyl acetoacetate, 141-97-9; 1,3-butadiene, 106-99-0.

Convergent Functional Groups. 2. Structure and Selectivity in Olefin Epoxidation with Peracids

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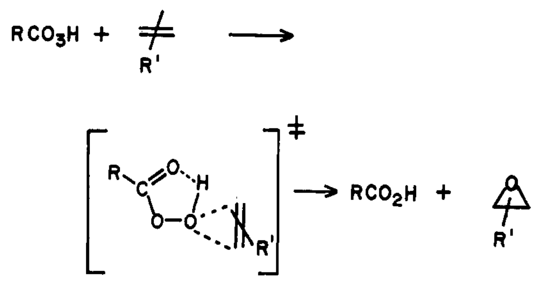
Problems associated with selectivity in olefin epoxidation with peracids are discussed, with special regard to cis/trans selectivity. The development of a new class of peracids is described in which steric effects become magnified and compete with electronic ones. These reagents show high selectivity for cis olefins in the presence of trans or 1,1-disubstituted derivatives. The possible origins of selectivity are outlined, and these are related to proposals concerning the transition structure for oxygen transfer with peracids.

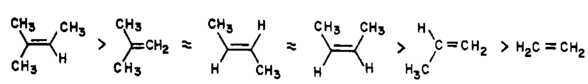
Introduction

Stereoelectronic effects[1] have come to dominate mechanistic thinking in this decade in much the same way as the Woodward–Hoffmann rules did the last one, with good reason. These effects provide a Rosetta stone for translating structure into reactivity. This article is concerned with these notions as they apply to the Prilaschajew reaction, i.e., the peracid epoxidation of olefins (eq 1).



(1)

This reaction has been the subject of numerous mechanistic enquiries,[2] the results of which are summarized in the equation above: intramolecular hydrogen bonding in the peracid fixes the orientation of the O–O bond; the olefin approaches the system along the line of the O–O bond as though an S_N2 reaction were being performed on the terminal oxygen;[3a] oxygen transfer occurs without detectable intermediates. One of the important synthetic consequences of such a reaction trajectory is that the reaction rate appears immune to steric effects. Little opportunity exists for interactions between groups on the olefin and the R of the peracids. Accordingly, most cis-disubstituted olefins react only slightly (1.1–2.2 times) faster than their trans counterparts,[3b] regardless of peracid structure, and 1,1-disubstituted olefins react at rates comparable to either the cis or trans isomers (eq 2; relative rates of olefin epoxidation with peracids[3c] are given below the structures).



230 22 20 22 1.0 .045 (2)

This consistency has permitted the reaction to survive as a practical synthetic method for some 75 years. The inefficiency of asymmetric peracids in providing optically active epoxides is also understandable from the transition structure of eq 1. An asymmetric environment provided by substituents at the α-carbon of a peracid is ill-placed to influence the approach and alignment of an olefin near the distal oxygen. In this respect, then, cis/trans selectivity

(1) Deslongchamps, P. "Stereoelectronic Effects in Organic Chemistry"; Pergamon Press: Oxford, 1983.

(2) For reviews with leading references see: Rebek, J., Jr. *Heterocycles* **1981**, *15*, 517–545; Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734–750.

(3) (a) See, for example: Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63–73 and literature cited therein. (b) Stumpf, W.; Rombusch, K. *Justus liebigs Ann. Chem.* **1965**, *687*, 136–199. (c) Swern, D. *Org. React.* **1953**, *7*, 378–433.

(4) (a) A preliminary account of this work has appeared: Rebek, J., Jr.; Marshall, L.; Wolak, R.; McManis, J. *J. Am. Chem. Soc.* **1984**, *106*, 1170–71; (b) Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985** *107*, 7426–7481.

