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# Observation of Periselectivity for the Cyclocoupling Reactions of 2-Oxyallyl Cation with Tricarbonyliron Complexes of Seven-Membered-Ring Unsaturated Compounds

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The 2-oxyallyl cation (**2**) showed significant differences of periselectivity in reactions between seven-membered-ring unsaturated compounds with masking and without masking by tricarbonyliron. The cation **2** reacted with tricarbonyl(cycloheptatriene)iron (**3**) to give a tricarbonyl-$\sigma,\pi$-allyl complex **5**. The structure of **5** was fully established by X-ray analysis. The oxidative degradation of **5** with *o*-chloranil afforded a single iron-free compound (**6**), which had inserted a carbonyl group. The cycloaddition of the cation **2** with 8-(4-chlorophenyl)-8-azaheptafulvene (**10**) gave a 1:1 adduct (**14**), which probably arose from the $[2_{\pi(3C)} + 8_{\pi}]$ adduct **13** via a 1,3 hydrogen shift. In contrast, the cycloaddition of the cation **2** with tricarbonyl[8-(4-chlorophenyl)-8-azaheptafulvene]iron (**11**) afforded a spiro-type adduct (**15**). The reaction of the cation **2** with tricarbonyl[*N*-(ethoxycarbonyl)azepine]iron (**17**), followed by oxidative degradation with *o*-chloranil, afforded a novel 1:1 adduct (**21**) in addition to compound **22**.

In the past decade, medium-ring polyenes have been used as the most suitable compounds for studying periselectivity, site selectivity, and regioselectivity in cycloadditions. Previously, we have investigated the factors influencing them in the cyclocoupling reactions of the 2-oxyallyl cation (**2**) with seven-membered-ring unsaturated compounds, cyclopentadienones, and fulvenes.[1]

Recent synthetic studies by Green et al.[2] and Gandolfi et al.[3] have shown that coordination of cyclic polyenes such as cycloheptatriene, 8-azaheptafulvene, *N*-(alkoxycarbonyl)azepine, and tropone to a tricarbonyliron unit can lead to significant changes in the reactivity and reaction patterns toward electrophilic reagents.

This paper deals with the role of tricarbonyliron complexes of these seven-membered-ring unsaturated compounds in the cyclocoupling reactions with the 2-oxyallyl cation (**2**). These results are discussed here in detail in comparison with the previous works.[1]

## Results and Discussion

**Cyclocoupling of the 2-Oxyallyl Cation (2) with Tricarbonyl(cycloheptatriene)iron (3).** The 2-oxyallyl cation (**2**),[1] generated from 2,4-dibromo-2,4-dimethylpentan-3-one (**1**) and $Fe_2(CO)_9$, reacted with tricarbonyl(cycloheptatriene)iron (**3**) to give a 1:1 adduct (**5**). The structure of the adduct **5** was assigned on the basis of spectroscopic data. The mass spectrum showed ions at *m/e* 344 ($M^+$), 316 ($M^+ - CO$), 288 ($M^+ - 2CO$), and 260 ($M^+ - 3CO$), and the IR spectrum exhibited a ketonic carbonyl band at 1695 $cm^{-1}$ in addition to iron carbonyl bands at 2080 and 1980 $cm^{-1}$. These spectral data suggested the formation of a 1:1 adduct, which is consistent with a tricarbonyliron group and a cyclohexanone moiety. In the $^1H$ NMR spectrum, the methine proton $H_j$ displayed a signal at $\delta$ 1.28 as a double doublet,[4] which was shielded to higher field due to its bearing an iron atom. In a decoupling experiment of $H_a$ and $H_f$, the methine proton $H_j$ appeared as a doublet. In the $^{13}C$ NMR spectrum, $C_j$ showed a signal at $\delta$ 19.7 as a doublet. However, the complete stereostructure, particularly the formation of the $\sigma$ bond and the conformation of the cyclohexanone moiety, was not established. Although there are now a number of reports describing the formal cycloaddition of several reactive dienophiles to medium-ring unsaturated compounds, structural assignments to certain of these adducts have frequently been founded upon chemical intuition and unproven assumptions rather than detailed structural information.[2]

Table I. Interatomic Distances (Å) and Their Estimated Standard Deviations for Complex 5

| | | | |
|---|---|---|---|
| Fe(1)–C(2) | 1.802 (4) | Fe(1)–C(4) | 1.771 (4) |
| Fe(1)–C(6) | 1.774 (4) | Fe(1)–C(8) | 2.163 (4) |
| Fe(1)–C(9) | 2.066 (4) | Fe(1)–C(10) | 2.124 (4) |
| Fe(1)–C(13) | 2.075 (4) | C(2)–O(3) | 1.136 (5) |
| C(4)–O(5) | 1.137 (5) | C(6)–O(7) | 1.138 (5) |
| C(8)–C(9) | 1.378 (6) | C(8)–C(14) | 1.508 (6) |
| C(9)–C(10) | 1.410 (6) | C(10)–C(11) | 1.505 (6) |
| C(11)–C(12) | 1.529 (6) | C(12)–C(13) | 1.499 (5) |
| C(12)–C(17) | 1.546 (6) | C(13)–C(14) | 1.529 (5) |
| C(14)–C(15) | 1.565 (6) | C(15)–C(16) | 1.530 (6) |
| C(15)–C(19) | 1.550 (6) | C(15)–C(20) | 1.534 (6) |
| C(16)–C(17) | 1.532 (6) | C(16)–O(18) | 1.212 (5) |
| C(17)–C(21) | 1.538 (7) | C(17)–C(22) | 1.524 (7) |

In order to clarify these obscurities and to account for the spectroscopic data, a single-crystal X-ray diffraction study was undertaken. The crystal structure was solved by the direct method. Refinement to an *R* factor of 3.3% was obtained by the method of least-squares on 1865 nonzero structure factors. The bond lengths and angles are listed in Tables I and II.

As can be seen in the computer-generated drawing[5] (Figure 1), adduct **5** is established to be a $\sigma,\pi$-allyliron tricarbonyl complex. The seven-membered ring C(8)–C(14) is bonded to the iron atom not only by a $\pi$-allyl linkage through C(8), C(9), and C(10) but also by a direct $\sigma$ bond between Fe and C(13), as evidenced by the sum of angles C(12)–C(13)–C(14), C(12)–C(13)–H(13), and C(14)–C(13)–H(13) being 346.8°. The configuration is roughly

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[1] (a) Ishizu, T.; Mori, M.; Kanematsu, K. *J. Org. Chem.* **1981**, *46*, 526–531. (b) Some of the work in this paper has appeared in a preliminary form: Ishizu, T.; Harano, K.; Yasuda, M.; Kanematsu, K. *Tetrahedron Lett.* **1981**, 1601–1604.

[2] (a) Green, M.; Heathcock, S.; Wood, D. C. *J. Chem. Soc., Dalton Trans.* **1973**, 1564–1569. (b) Paquette, L. A.; Ley, S. V.; Maiorana, S.; Schneider, D. F.; Broadhust, M. J.; Boggs, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 4658–4667.

[3] Gandolfi, R.; Toma, L. *Tetrahedron* **1980**, *36*, 935–941.

[4] Aumann, V. R. *Angew. Chem.* **1971**, *83*, 175–176, 176–177. Moriarty, R. M.; Yeh, C.; Ramey, K. C. *J. Am. Chem. Soc.* **1971**, *93*, 6709–6710.

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Table II. Bond Angles (deg) and Their Estimated Standard Deviations for Complex 5

| | | | |
|---|---|---|---|
| C(2)-Fe(1)-C(4) | 95.5 (2) | C(2)-Fe(1)-C(6) | 93.4 (2) |
| C(2)-Fe(1)-C(8) | 107.7 (2) | C(2)-Fe(1)-C(9) | 89.5 (2) |
| C(2)-Fe(1)-C(10) | 99.2 (2) | C(4)-Fe(1)-C(6) | 98.8 (2) |
| C(4)-Fe(1)-C(8) | 152.7 (2) | C(4)-Fe(1)-C(9) | 131.6 (2) |
| C(4)-Fe(1)-C(10) | 92.6 (2) | C(6)-Fe(1)-C(8) | 94.0 (2) |
| C(6)-Fe(1)-C(9) | 129.0 (2) | C(6)-Fe(1)-C(10) | 162.2 (2) |
| C(8)-Fe(1)-C(9) | 38.0 (2) | C(8)-Fe(1)-C(10) | 70.2 (2) |
| C(9)-Fe(1)-C(10) | 39.3 (2) | Fe(1)-C(2)-O(3) | 178.4 (4) |
| Fe(1)-C(4)-O(5) | 177.4 (4) | Fe(1)-C(6)-O(7) | 178.0 (4) |
| C(9)-C(8)-C(14) | 125.3 (4) | C(8)-C(9)-C(10) | 124.4 (4) |
| C(9)-C(10)-C(11) | 124.1 (4) | C(10)-C(11)-C(12) | 114.0 (4) |
| C(11)-C(12)-C(13) | 109.7 (3) | C(11)-C(12)-C(17) | 111.5 (3) |
| C(13)-C(12)-C(17) | 112.4 (3) | C(12)-C(13)-C(14) | 114.0 (3) |
| C(8)-C(14)-C(13) | 102.1 (3) | C(8)-C(14)-C(15) | 116.8 (3) |
| C(13)-C(14)-C(15) | 118.5 (3) | C(14)-C(15)-C(16) | 114.7 (3) |
| C(14)-C(15)-C(19) | 108.8 (3) | C(14)-C(15)-C(20) | 111.5 (3) |
| C(16)-C(15)-C(19) | 105.8 (3) | C(16)-C(15)-C(20) | 108.2 (3) |
| C(19)-C(15)-C(20) | 107.4 (4) | C(15)-C(16)-C(17) | 121.3 (4) |
| C(15)-C(16)-O(18) | 119.5 (4) | C(17)-C(16)-O(18) | 119.2 (4) |
| C(12)-C(17)-C(16) | 107.1 (3) | C(12)-C(17)-C(21) | 110.2 (4) |
| C(12)-C(17)-C(22) | 111.6 (4) | C(16)-C(17)-C(21) | 109.0 (4) |
| C(16)-C(17)-C(22) | 110.1 (4) | C(21)-C(17)-C(22) | 108.9 (4) |

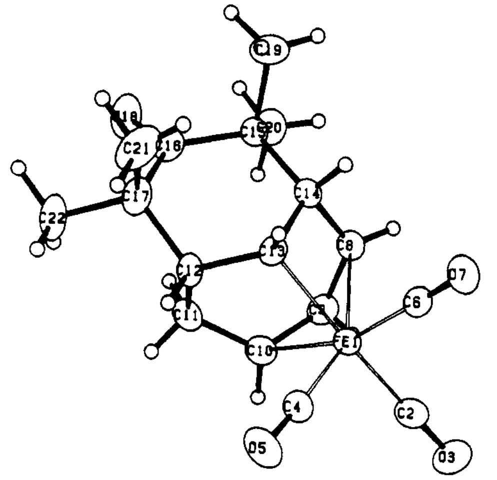
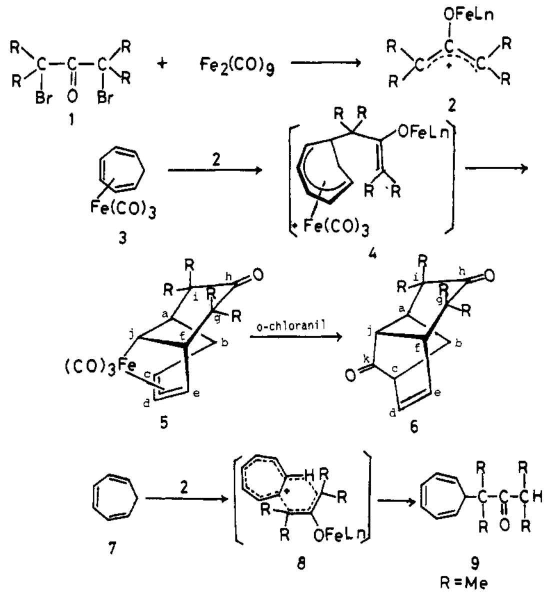
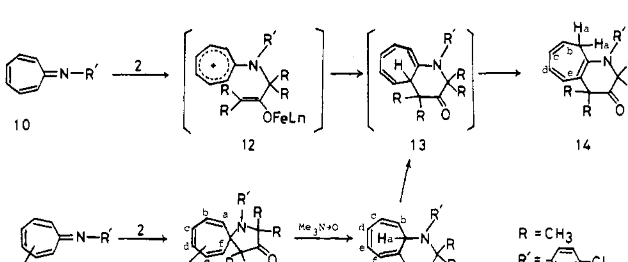


**Figure 1.** Drawing indicating the numbering sequence used in this paper for the 22 independent nonhydrogen atoms. The thermal ellipsoids are drawn at the 30% probability level, with exception of those for the hydrogen atoms which have been reduced for clarity.

Scheme I



Scheme II



octahedral.[6] Interbond angles at sp$^2$ carbons [C(14)-C(8)-C(9), 125.3°; C(8)-C(9)-C(10), 124.4°; C(9)-C(10)-C(11), 124.1°] deviate by 5.3°, 4.4° and 4.1°, respectively, from the usual angles of 120°, and the C(8)-C(9) and C(9)-C(10) bond lengths, 1.38 and 1.41 Å, respectively, are longer than the normal value of a double bond length, 1.34 Å. The six-membered ring formed by C(15), C(16), and C(17) derived from the 2-oxyallyl cation (2) has a chair conformation: the carbon atoms C(15) and C(12) lie 0.2 Å above and 0.68 Å below the best plane through atoms C(13), C(14), C(16), and C(17), respectively. The coupling constants of the $^1H$ NMR spectrum for compound **5** ($J_{a,j}$ = 7.0, $J_{f,j}$ = 14.0 Hz) are quite consistent with the dihedral angles of the X-ray results (44° and 23°). Furthermore, the carbonyl group of the cyclohexanone moiety in the IR (1695 cm$^{-1}$) was also quite consistent with the angle of the X-ray results (121.3°, which is a small deviation from the unstrained angle of 120°). The formation of the adduct **5** after a reaction time of 1 h at 50 °C in solvents of different polarity such as *n*-hexane, benzene, and tetrahydrofuran was monitored by thin-layer chromatography (TLC), and the yield was increased in proportion with the $E_T$ values of the solvent[7] (see Experimental Section). This result suggested that the reaction proceeded in a stepwise fashion via the zwitterion **4**. By contrast, the reaction of the 2-oxyallyl cation (**2**) with cycloheptatriene (**7**) afforded an ene-type adduct (**9**). This reaction was suggested to proceed by a concerted process via the cyclic transition state **8**.[1]

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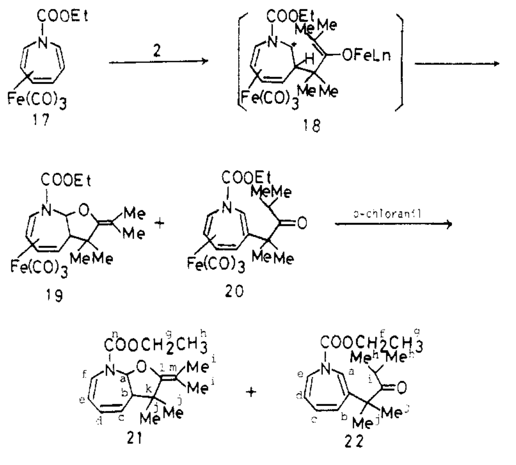
(6) Smith, D. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1962**, *84*, 1743–1744.

(7) (a) Dimroth, K.; Reinhardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1–29. (b) Reinhardt, C. *Angew. Chem.* **1965**, *77*, 30–40.

Scheme III



Oxidative degradation of complex **5** with *o*-chloranil afforded a single iron-free product (**6**). The elemental analysis and the mass spectrum (*m*/*e* 232 ($M^+$)) indicated that a carbonyl insertion had taken place during oxidation (Scheme I). The IR spectrum showed two carbonyl absorptions at 1750 (cyclopentanone) and 1690 $cm^{-1}$ (cyclohexanone). Furthermore, the $^1H$ NMR and $^{13}C$ NMR spectral data of **6** supported the structure **6** as depicted in Scheme I.

**With 8-(4-Chlorophenyl)-8-azaheptafulvene (10) and Tricarbonyl[8-(4-chlorophenyl)-8-azaheptafulvene]iron (11).** The cyclocoupling reaction of **2** with **10**[8] afforded a 1:1 adduct (**14**, Scheme II).

The mass spectrum of adduct **14** showed iron at *m*/*e* 327, suggesting the formation of a 1:1 adduct, and the IR spectrum exhibited the six-membered ketone at 1719 $cm^{-1}$. In the $^1H$ NMR spectrum, the methylene protons $H_a$ appeared at $\delta$ 2.16 as a doublet. The adduct **14** was presumably formed in a stepwise manner via intermediacy of tropylium cation **12** followed by ring closure and a subsequent 1,3 hydrogen shift. The similar reaction and 1,3 hydrogen shift was reported previously.[1] In contrast, **2** reacted with **11** to give a spiro-type adduct (**15**, Scheme II). The $^1H$ NMR pattern of the adduct **15** was similar to that of the adduct with diphenylnitrilimine.[3] The tricarbonyliron group of adduct **15** was then easily removed on treatment with trimethylamine *N*-oxide to give a $[2_{\pi(3C)} + 8_\pi]$ adduct (**16**) in a fairly good yield. In the $^1H$ NMR spectrum, methine proton $H_a$ showed doublet with a downfield shift at $\delta$ 3.26 due to the influence of the adjacent nitrogen atom.

Compound **14** was also obtained quantitatively by dissolving compound **16** in trifluoroacetic acid and by neutralizing the solution subsequently at −10 °C with triethylamine in acetonitrile. The $^1H$ NMR spectral pattern of the compound derived from **16** agreed perfectly with that of the adduct of **2** with **10**. A similar transformation was performed with the $^1H$ NMR spectrum in $CF_3COOD$ by Gandolfi et al.[3]

**With Tricarbonyl[*N*-(ethoxycarbonyl)azepine]iron (17).** The 2-oxyallyl cation (**2**) reacted with **17** to give a mixture of adducts **19** and **20**. Successive oxidative degradation of the mixture with *o*-chloranil afforded a mixture of **21** and **22** as shown in Scheme III.

In the $^1H$ NMR spectrum of **21**, the methine protons $H_b$ and $H_a$ displayed signals at $\delta$ 3.46 as a double doublet and at $\delta$ 6.36 as a doublet, respectively. The $H_a$ proton was influenced by the adjacent nitrogen atom and the vinyl ether moiety. In a decoupling experiment, the two methine protons, $H_a$ and $H_b$, appeared as a singlet and doublet, respectively. Furthermore, in the $^{13}C$ NMR spectrum, $C_m$ appeared at 80.2 ppm as a singlet, which was shielded to higher field because of the $\beta$-position of the vinyl ether moiety.[9]

The $^1H$ NMR spectrum of **22** exhibited characteristic signals of methine protons $H_j$ and $H_a$ as a heptet at $\delta$ 2.94 and a singlet at $\delta$ 6.92, respectively.

The reaction was expected to proceed by a stepwise mechanism involving the zwitterion intermediate **18**, which would be formed by initial electrophilic attack of the cation **2** on the negatively charged carbon at C-3 due to the enamine moiety of **17**. Further ring closure produced the adduct **21** by nucleophilic attack of enolate anion moiety of **18**. On the other hand, a hydrogen shift from the same intermediate **18** would give compound **22**.

Finally, the 2-oxyallyl cation (**2**) was inert to tricarbonyl(tropone)iron. However, the cation (**2**) did react with tropone to give the $[2_{\pi(3C)} + 8_\pi]$ adduct.[1] From these results, it is pointed out that the cyclocoupling reaction of the 2-oxyallyl cation (**2**) with seven-membered-ring unsaturated compounds is expected to proceed by the preference of the cation LUMO and the polyene HOMO interaction rather than the inverse interaction.[10] However, the complex of tropone with a low HOMO energy level[3] shows little reactivity toward **2** in the coupling reaction.

## Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. $^1H$ NMR spectra were taken with a JEOL PS-100 spectrometer with $Me_4Si$ as an internal standard; chemical shifts are expressed in $\delta$ values. $^{13}C$ NMR spectra were recorded on a JEOL FX-100 with $Me_4Si$ as an internal standard. IR spectra were taken with a JASCO DS-701G infrared spectrophotometer. Mass spectra were obtained with a JEOL-01SG double-focusing spectrometer operating at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200 °C.

**Reaction of the 2-Oxyallyl Cation (2) with Tricarbonyl(cycloheptatriene)iron (3).** A mixture of $Fe_2(CO)_9$ (18.4 g), **1** (11.4 g), and **3** (6.5 g) in 100 mL of dry benzene was stirred at 50 °C for 8 h. The mixture was filtered and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene to give a crude product. The reaction yields of **5** were measured with an Iatron TH-10/FID analyzer (Iatron Laboratories, Inc.). The product was recrystallized from *n*-hexane to give **5** (1.9 g, 20%) as pale yellow crystals: mp 88–89 °C, mass spectrum, *m*/*e* 344 ($M^+$), 316 ($M^+ - CO$), 288 ($M^+ - 2CO$), 260 ($M^+ - 3CO$); IR (Nujol) 2080, 1980 ($Fe(CO)_3$), 1695 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.92, 1.00, 1.14, and 1.16 (s, 12 H, 4 $CH_3$), 1.28 (dd, 1 H, $H_j$, $J_{aj} = 7$ Hz, $J_{fj} = 14$ Hz), 1.96–2.16 (m, 1 H, $H_b$), 2.28 (ddd, 1 H, $H_a$, $J_{ab} = 1$ Hz, $J_{ab'} = 6$ Hz), 2.36–2.72 (m, 1 H, $H_f$), 3.05 (ddd, 1 H, $H_{b'}$, $J_{bb'} = 1$ Hz, $J_{b'c} = 9.5$ Hz), 4.24–4.56 (m, 3 H, $H_c$, $H_d$, $H_e$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 19.7 (d, $C_j$), 22.5, 25.1, 25.6, and 31.7 (q, $4CH_3$), 33.2 (t, $C_b$), 47.5, 49.7 (s, $C_g$, $C_i$), 52.3, 59.5 (d, $C_a$, $C_f$), 66.0, 71.5 (d, $C_c$, $C_e$), 97.0 (d, $C_d$), 202.7, 213.3, 214.3 (s, ligand carbonyl), 220.2 (s, $C_h$). Anal. Calcd for $C_{17}H_{20}O_4Fe$: C, 59.3; H, 5.9. Found: C, 59.3; H, 5.9.

**Oxidative Degradation of 5 with *o*-Chloranil.** To a solution of *o*-chloranil (0.46 g) in dry chloroform (10 mL) was added a solution of **5** (0.35 g) in the same solvent (5 mL) dropwise at room temperature under vigorous stirring, and the mixture was then stirred for 24 h. The mixture was filtered and evaporated under

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[9] (a) Maciel, G. E. *J. Phys. Chem.* **1965**, *69*, 1947–1951. (b) Hatada, K.; Nagata, K.; Yuki, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3195–3198, 3267–32689.

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reduced pressure. The residue was chromatographed on silica gel with chloroform to give crude product. The product was recrystallized from *n*-hexane to give **6** (0.11 g, 47%) as colorless crystals: mp 93–95 °C; mass spectrum *m/e* 232 ($M^+$); IR (KBr) 1750 (cyclopentanone), 1690 (cyclohexanone) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.11, 1.17, 1.31, and 1.34 (s, 12 H, $4CH_3$), 1.72 (ddd, 1 H, $H_b$, $J_{ab} = 1$ Hz, $J_{bc} = 7$ Hz, $J_{bb'} = 1$ Hz), 2.18 (ddd, 1 H, $H_a$, $J_{ab'} = 6.5$ Hz, $J_{aj} = 11$ Hz), 2.36–2.48 (m, 1 H, $H_j$), 2.52–2.64 (m, 1 H, $H_c$), 3.04 (ddd, 1 H, $H_{b'}$, $J_{b'c} = 4.5$ Hz), 3.14–3.28 (m, 1 H, $H_f$), 5.62 (dd, 1 H, $H_e$, $J_{de} = 9.5$ Hz, $J_{ef} = 3.5$ Hz), 6.14 (dd, 1 H, $H_d$, $J_{cd} = 7$ Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 23.4, 24.5, 28.1, and 31.0 (q, $4CH_3$), 36.0 (t, $C_b$), 43.6, 44.1, and 45.9 (d, $C_a$, $C_j$, $C_f$), 45.1, 47.2 (s, $C_g$, $C_i$), 57.2 (d, $C_c$), 127.0, 135.6 (d, $C_d$, $C_e$), 213.2 (s, $C_k$), 217.3 (s, $C_h$). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.6; H, 8.7. Found: C, 77.4; H, 8.6.

**Reaction of the 2-Oxyallyl Cation (2) with 8-(4-Chlorophenyl)-8-azaheptafulvene (10).** A mixture of $Fe_2(CO)_9$ (4.24 g), **1** (2.54 g), and **10** (1.0 g) in 20 mL of dry benzene was stirred at 50 °C for 8 h. The mixture was filtered and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene to give **14** (0.56 g, 37%) as a pale yellow oil: bp 130 °C (2 mm); exact mass 327.1357 (calcd 327.1360); IR (neat) 1719 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.25 (s, 6 H, $2CH_3$), 1.41 (s, 6 H, $2CH_3$), 2.16 (d, 2 H, 2 $H_a$, $J_{ab} = 7$ Hz), 5.10 (dd, 1 H, $H_b$, $J_{bc} = 15.5$ Hz), 6.12–6.32 (m, 1 H, $H_c$), 6.44 (dd, 1 H, $H_d$, $J_{cd} = 1$ Hz, $J_{de} = 5$ Hz), 6.60–6.78 (m, 1 H, $H_e$), 7.00–7.36 (m, 4 H, aromatic H).

**Reaction of the 2-Oxyallyl Cation (2) with Tricarbonyl[8-(4-chlorophenyl)-8-azaheptafulvene]iron (11).** A mixture of $Fe_2(CO)_9$ (1.28 g), **1** (0.77 g), and **15** (0.5 g) in 15 mL of dry benzene was stirred at 45 °C for 8 h. The mixture was filtered and evaporated under reduced pressure to give a crude product. The product was recrystallized from *n*-hexane to give **15** (0.14 g, 22%) as pale yellow crystals: mp 185–187 °C; mass spectrum, *m/e* 439 ($M^+ - CO$), 383 ($M^+ - 3CO$); IR (Nujol) 2080, 1990, and 1980 ($Fe(CO)_3$), 1743 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.80, 1.13, 1.18, and 1.48 (s, 12 H, $4CH_3$), 2.92–3.20 (m, 2 H, $H_c$, $H_f$), 5.24–5.44 (m, 3 H, $H_a$, $H_d$, $H_e$), 5.96 (dd, 1 H, $H_b$, $J_{bc} = 11$ Hz, $J_{ab} = 8$ Hz), 7.08–7.36 (m, 4 H, aromatic H). Anal. Calcd for $C_{23}H_{22}O_4NClFe$: C, 59.1; H, 4.7; N, 3.0. Found: C, 59.0; H, 4.9; N, 3.0.

**Oxidative Degradation of 15 with Trimethylamine *N*-Oxide.** A mixture of **15** (0.5 g) and trimethylamine *N*-oxide (0.64 g) in acetonitrile (15 mL) was stirred for 24 h at room temperature. The mixture was then diluted with dichloromethane, filtered, washed with water, and dried to give a crude product. The product was recrystallized from *n*-hexane to give **16** (0.25 g, 72%) as colorless crystals: mp 119–121 °C; mass spectrum, *m/e* 327 ($M^+$); IR (KBr) 1719 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.08, 1.18, 1.36, and 1.60 (s, 12 H, $4CH_3$), 3.26 (d, 1 H, $H_a$, $J_{ab} = 5$ Hz), 5.10 (dd, 1 H, $H_b$, $J_{bc} = 9$ Hz), 5.88–6.09 (m, 1 H, $H_c$), 6.09–6.22 (m, 1 H, $H_d$), 6.64–6.72 (m, 2 H, $H_e$, $H_f$), 7.04–7.32 (m, 4 H, aromatic H). Anal. Calcd for $C_{20}H_{22}ONCl$: C, 73.3; H, 6.8; N, 4.3. Found: C, 73.2; H, 6.7; N, 4.2.

**Isomerization of Adduct 16 to Adduct 14.** To a solution of triethylamine (2 mL) in acetonitrile (10 mL) was added a solution of **16** (0.05 g) in trifluoroacetic acid (1 mL) dropwise at −10 °C under vigorous stirring. The mixture was diluted with dichloromethane, washed with water, dried, and evaporated to give **14** quantitatively as a pale yellow oil.

**Reaction of the 2-Oxyallyl Cation (2) with Tricarbonyl[*N*-(ethoxycarbonyl)azepine]iron (17).** A mixture of $Fe_2(CO)_9$ (6.3 g), **1** (4.1 g), and **17** (1.5 g) in 30 mL of dry benzene was stirred at 60 °C for 8 h. The mixture was filtered and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene to give a mixture of **19** and **20** as a yellow oil, mass spectrum, *m/e* 417 ($M^+$).

**Oxidative Degradation of a Mixture of 19 and 20 with *o*-Chloranil.** To a solution of *o*-chloranil (1.18 g) in dry chloroform (20 mL) was added a solution of a mixture of **19** and **20** (1.0 g) in the same solvent (10 mL) dropwise at room temperature under vigorous stirring, and the mixture was then stirred for 24 h. The mixture was filtered and evaporated under reduced pressure. The residue was chromatographed on silica gel with chloroform to give two crude products. One of them was recrystallized from *n*-hexane to give **21** (0.14 g, 21%) as colorless crystals (silica gel, chloroform, $R_f$ 0.83). The other product (**22**) was recrystallized from benzene to give **22** (0.16 g, 24%) as pale yellow crystals (silica gel, chloroform, $R_f$ 0.69).

For compound **21**: mp 195–197 °C; mass spectrum, *m/e* 277 ($M^+$); IR (KBr) 1728 (NCO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.08 (t, 3 H, $CH_3^h$, $J_{gh} = 7.5$ Hz), 1.26 (s, 6 H, $2CH_3^j$), 1.36 (s, 3 H, $CH_3^i$), 1.68 (s, 3 H, $CH_3^i$), 3.46 (dd, 1 H, $H_b$, $J_{ab} = 10$ Hz, $J_{bc} = 8$ Hz), 4.04 (q, 2 H, $CH_2^g$), 5.46 (dd, 1 H, $H_e$, $J_{de} = 5.5$ Hz, $J_{ef} = 8.5$ Hz), 5.76 (dd, 1 H, $H_c$, $J_{cd} = 11.5$ Hz), 6.02 (dd, 1 H, $H_d$), 6.36 (d, 1 H, $H_a$), 6.48 (d, 1H, $H_f$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.0 (q, $C_h$), 22.6, 23.0, 24.0, and 25.7 (q, $4CH_3$), 48.8 (d, $C_b$), 50.5 (s, $C_k$), 62.6 (t, $C_g$), 80.2 (s, $C_m$), 95.8 (d, $C_a$), 107.9 (d, $C_e$), 118.1 (s, $C_1$), 127.7, 129.3, and 129.4 (d, $C_c$, $C_d$, and $C_f$), 154.1 (s, $C_n$). Anal. Calcd for $C_{16}H_{23}O_3N$: C, 69.3; H, 8.4; N, 5.1. Found: C, 69.2; H, 8.3; N, 5.1.

For compound **22**: mp 232–233 °C; mass spectrum, *m/e* 277 ($M^+$); IR (KBr) 1729 (NCO), 1705 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.76 (d, 3 H, $CH_3^h$, $J_{hi} = 7$ Hz), 0.98 (d, 3 H, $CH_3^h$, $J_{hi} = 7$ Hz), 1.28, 1.32 (s, 6 H, $2CH_3^j$), 1.46 (t, 3 H, $CH_3^g$, $J_{fg} = 7$ Hz), 2.94 (h, 1 H, $H_j$), 4.36 (q, 2 H, $CH_2^f$), 5.12 (m, 1 H, $H_d$), 5.36–5.56 (m, 1 H, $H_c$), 5.58–5.80 (m, 1 H, $H_b$), 6.64 (m, 1 H, $H_e$), 6.92 (s, 1 H, $H_a$). Anal. Calcd for $C_{16}H_{23}O_3N$: C, 69.3; H, 8.4; N, 5.1. Found: C, 69.3; H, 8.5; N, 4.9.

**Measurements of Yields of Reaction of the 2-Oxyallyl Cation (2) with Tricarbonyl(cyclohepetatriene)iron (3).** The mixtures of $Fe_2(CO)_9$ (0.182 g, $5.0 \times 10^{-4}$ M), **1** (0.136 g, $5.0 \times 10^{-4}$ M), **3** (0.116 g, $5.0 \times 10^{-4}$ M), and $\beta$-methoxynaphthalene (0.079 g, $5.0 \times 10^{-4}$ M) as an internal standard in 5 mL of the various solvents [dry tetrahydrofuran ($E_T = 37.4$), dry benzene ($E_T = 34.5$), and dry *n*-hexane ($E_T = 30.9$)] were stirred at 50 ± 1 °C for 1 h in each case. The mixture was cooled to 0 °C followed by filtering of the insoluble ferric bromide. The yields were 29% in dry tetrahydrofuran, 16% in dry benzene, and 10% in dry *n*-hexane.

**X-ray Crystallographic Study of the Complex 5.** Suitable single crystals of the complex **5** were obtained by slow crystallization from a benzene–hexane solution. A crystal of the complex **5** with approximate dimensions 0.6 × 0.45 × 0.4 mm was mounted on a glass fiber with epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P\bar{1}$ four-circle diffractometer equipped with a graphite monochromator and using Mo K$\alpha$ radiation.

Fifteen reflections whose $2\theta$ values ranged from 6.1 to 26.1° were used in the least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were $a = 9.840$ (6) Å, $b = 12.176$ (6) Å, $c = 8.076$ (4) Å, $\alpha = 95.43$ (4)°, $\beta = 118.31$ (3)°, $\gamma = 105.91$ (5)°, and $V = 791$ (1) $Å^3$. The calculated density of 1.445 g $cm^{-3}$ for two formula units per unit cell agrees with the experimental density of 1.420 $gcm^{-3}$ measured by the flotation method with a mixture of $H_2O$ and KI. The space group $P\bar{1}$ was selected from the number of molecules per unit cell ($Z = 2$) and was later confirmed in the course of the structure refinement.

Intensity data were collected by using $\theta$–$2\theta$ scans to a limit of $2\theta = 50°$ with X-ray source and monochrometer settings identical with those used for determination of the unit cell parameters. A variable scan rate from 24.0 to 4.0 $min^{-1}$ was used. The eight reflections whose peak counting rate exceeded 50000 counts/s were remeasured with a lower beam intensity to minimize counting losses. Three reflections, monitored at regular intervals during the data collection, showed no significant variation in intensity.

Of 2096 independent reflections, 1865 were treated as observed ($I > 2.3\sigma(I)$). The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption.

Observed structure factors were converted into normalized structure factor amplitudes, $|E|$ values, by use of the scale factor and overall temperature factor obtained from Wilson's statistics.

The structure was solved by the direct method by using the MULTAN 78[11] program. An $E$ map calculated with 463 signed $E$'s ($|E| \geq 1.2$) which gave a combined figure of merit of 2.370 revealed the positions of 25 of the nonhydrogen atoms. Nine cycles of block-diagonal least-squares of minimizing of $\sum(|F_o| - k|F_c|)^2$ by

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varing the positions and isotropic vibrational amplitudes of the C, O, and Fe atoms led to $R = 0.089$. Six further cycles of least-squares refinement of the atomic parameters with anisotropic vibrational amplitudes for the C, O, and Fe atoms converged to $R = 0.068$. A difference Fourier map calculated at this stage revealed peaks of density appropriate to all hydrogen atoms. Keeping the vibrational amplitudes for the hydrogens fixed ($B(\mathrm{H}) = B(\mathrm{C}) + 1.0\ \text{Å})^2$ and refining with anisotropic $U$'s for all the C, O, and Fe atoms, we obtained a final $R$ of 0.033. The atomic scattering factors were taken from the literature.[12]

All the calculations were performed on the FACOM M-200 computer in the computer center of Kyushu University with the Universal Crystallographic Computation Program System UNICS II.[13]

**Registry No.** **1**, 17346-16-6; **3**, 36343-88-1; **5**, 78149-25-4; **6**, 78109-52-1; **10**, 62515-93-9; **11**, 78184-56-2; **14**, 78109-53-2; **15**, 78149-18-5; **16**, 78109-54-3; **17**, 12193-69-0; **19**, 78128-45-7; **20**, 78128-46-8; **21**, 78109-55-4; **22**, 78109-56-5; $Fe_2(CO)_9$, 15321-51-4.

**Supplementary Material Available:** Selected torsion angles (Table III), atomic parameters (Table IV), and coordinates for hydrogen atoms (Table V) (3 pages). Ordering information is given on any current masthead page.

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# Studies of Tertiary Amine Oxides. 4. Thermal Rearrangement of *N*-Aryl Amine Oxides to *O*-Arylhydroxylamines

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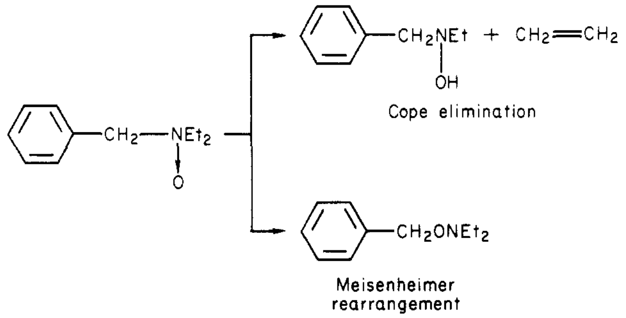
Substituted *N*-aryl cyclic amine oxides undergo novel thermal rearrangement to *O*-arylhydroxylamines. Electron-withdrawing substituents are essential for the rearrangement and must be ortho or para relative to the $\gt N{\rightarrow}O$ function. The mechanism of the rearrangement is best described by an intramolecular cyclic process. Kinetic results are in agreement with the cyclic process but are inconsistent with a homolytic dissociation–recombination mechanism.

Tertiary amine *N*-oxides (**1**) are a class of organic compounds that have received considerable attention in part because of their role in the microsomal[1] and plant[2] metabolism of tertiary amines and in part because of the interesting thermal rearrangement they undergo to the corresponding *O*-alkylhydroxylamines **2** (eq 1).

$$\underset{\mathbf{1}}{R_1R_2R_3N{\rightarrow}O} \rightarrow \underset{\mathbf{2}}{R_1R_2NOR_3} \qquad (1)$$

Meisenheimer et al.[3] were the first to recognize this reaction, which then became known as the Meisenheimer rearrangement. However, with these *N*-oxides having a β-hydrogen atom, an elimination reaction,[4] often referred to as the Cope elimination, might take place, yielding an olefin. For such compounds, elimination and isomerization are often found to be competitive, and *N*,*N*-diethylbenzylamine *N*-oxide (**3**), for example, on being heated afforded *N*-ethyl-*N*-benzylhydroxylamine, ethylene, and *O*-benzyl-*N*,*N*-diethylhydroxylamine (**4**) (Scheme I).

Scheme I



**4**

The type of group which could migrate in the Meisenheimer rearrangement ($R_3$ in eq 1) is rather closely defined. The groups that are known to show a tendency for migration from N to O include allyl,[5] benzyl,[6–9] neopentyl,[10] tetrachloropyridyl,[11] and homoadamantyl.[12] We have recently[13] reported on the migration of a benzene nucleus from N to O in substituted dimethylaniline oxides. This paper describes the scope and limitations of this type of migration.

## Results and Discussion

**Syntheses.** The tertiary amines **5** were prepared by reaction of the appropriate secondary amine and *o*- or

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