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IRON CARBONYL PROMOTED REACTION OF α,α'-DIBROMO KETONES AND ISOBUTYLENE. AN ENE REACTION INVOLVING ALLYLIC CATIONS[1]

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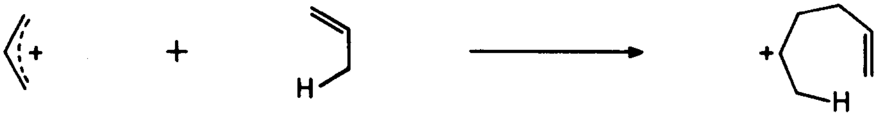
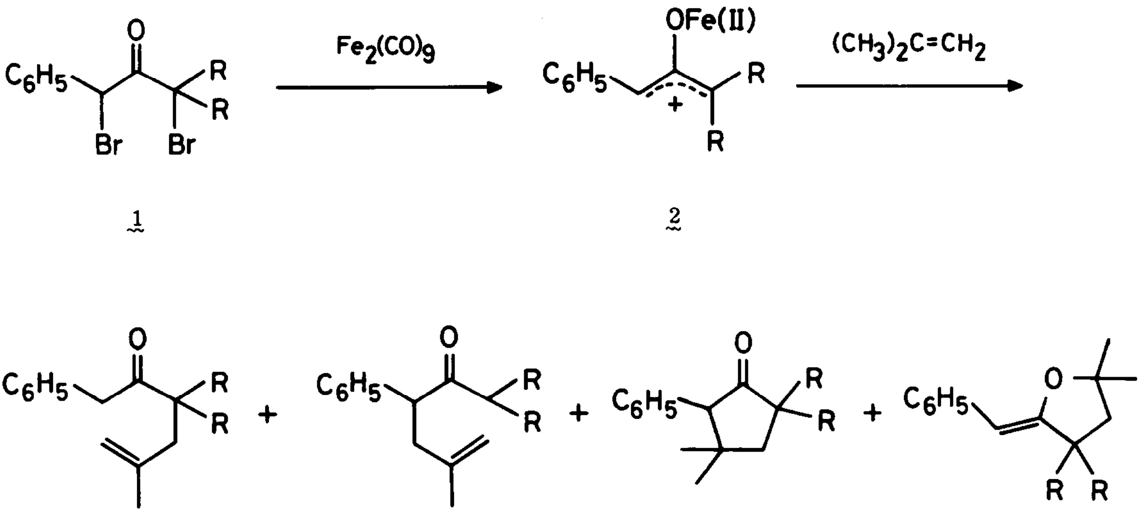
The title reaction, unlike the 3 + 2 reaction with arylated olefins[2] or enamines[3] as the olefinic substrate, proceeds very reluctantly. From mechanistic point of view, however, the reaction is worth noting, since it presents the first example of ene reaction[4] that involves an allylic cation as an enophile.



First, the reactive oxyallyl--Fe(II) species 2a was generated in situ from the corresponding dibromo ketone 1a and $Fe_2(CO)_9$ (1:1.2 molar ratio, benzene, 55 °C)[5] and trapped with a large excess of isobutylene. The 1:1 adducts obtained were 3a, 4a, 5a, and 6a (35% total yield, 52:5:14:29 ratio).[6] In a similar manner, the $Fe_2(CO)_9$ aided reaction of 2b and isobutylene afforded a mixture of the adducts 3b and 5b (5.5% yield, 9:91 ratio).[7,8] Any other 1:1 adducts were not detected in the crude reaction mixtures by GC--MS analysis.

The open-chain adducts 3 and 4 are products arising from ene reaction of the allyl cations (2) and isobutylene. Apparently the oxygen function at the central sp^2-carbon of 2 facilitates the heretofore unknown type of reaction. The selectivity is characterized by the preferential introduction of methallyl moiety to the non-phenylated carbon. The cyclopentanone 5 is a product resulting from stepwise 3 + 2 cycloaddition of 2 across the olefinic substrate.[2,3] Notably, electrophilic olefinic substitution products (open-chain internal olefins)[2] were not formed at all.

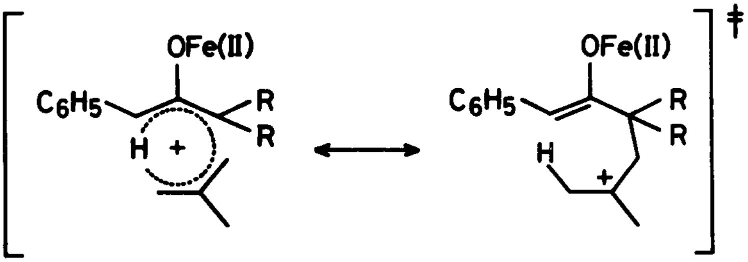
If operation of a single mechanism is assumed for this ene reaction, the observations are best accounted for in terms of a concerted [$_\sigma 2 + {}_\pi 2 + {}_\pi 2$] mechanism. The major or exclusive adduct arises via the seven-membered, six-electron transition state 7. Here approximation of the electronic nature by that of the canonical form 8 can well explain the unique regioselectivity; its cationic part is a stable tertiary carbocation and the enolate moiety is sufficiently



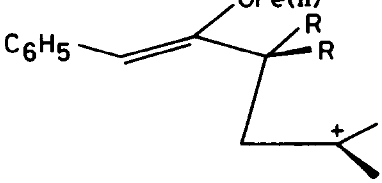
1 2

3 4 5 6

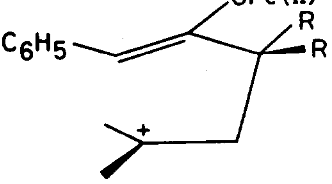
a: R = CH_3 b: R = H



7 8



9Z



9U

stabilized by phenyl group.[9] Alternative stepwise mechanism involving the Z-shaped zwitterion **9Z** can be excluded by the absence of the electrophilic olefinic substitution products. The U-shaped zwitterion **9U** (intermediate for the stepwise 3 + 2 cycloaddition) seems also unlikely to be involved. The relative ease with which such intermediate cyclizes to a cyclopentanone and leaks into an ene product through prototropy, we feel, is little affected by whether R is methyl or hydrogen, in conflict with the experimental findings. In fact, on going from **2a** to **2b**, the cyclopentanone/ene product ratio changed by a factor of 38![10] In usual the 3 + 2 reaction of oxyallyls (particularly with aromatic olefins[2]) via the zwitterions of type **9U** suffers severely steric screening effect,[11] while the concerted reactions such as 3 + 4 cycloaddition with 1,3-dienes are little influenced by such steric hindrance because of the relatively loose atomic arrangements in the transition states.[9,12,13] In the 3 + 2 reaction, electronic effects, particularly stabilities of the ionic centers of the intermediates, are also to be considered.[9] In the transformation **2a** → **9U**, the cationic center moves from tertiary to tertiary, whereas during the reaction **2b** → **9U** the favorable primary to tertiary change is involved. As such, **2a** gave the ene products predominantly over the 3 + 2 product, and reaction of **2b** exhibited the opposite selectivity.

ACKNOWLEDGMENT. Financial support by a grant from Ministry of Education (No. 203014) of the Japanese Government is gratefully acknowledged.

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5. R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, J. Am. Chem. Soc., **94**, 7202 (1972); R. Noyori, Y. Hayakawa, H. Takaya, S. Murai, R. Kobayashi, and N. Sonoda, ibid., in press.
6. All IR (cm^{-1}) and NMR data (δ) were taken in CCl_4. **3a**: IR 1714 (C=O), 890 ($=CH_2$); NMR 1.13 (s, $2CH_3$), 1.64 (br s, $=CCH_3$), 2.32 (br s, $=CCH_2$), 3.70 (s, $C\underline{H}_2C_6H_5$), 4.12, 4.29 (m, 1H each, $=CH_2$), 7.0—7.3 (m, C_6H_5); mass m/e 216 (M^+). **4a**: IR 1714 (C=O), 890

($=CH_2$); NMR 0.86, 1.03 (d, 3H each, *J* = 7 Hz, $CH(C\underline{H}_3)_2$), 1.65 (br s, $=CCH_3$), 2.1–2.9 (m, $C\underline{H}(CH_3)_2$ and $=CCH_2$), 3.88 (t, *J* = 7 Hz, $C\underline{H}C_6H_5$), 4.56, 4.63 (m, 1H each, $=CH_2$), 7.0–7.3 (m, C_6H_5); mass *m/e* 216 (M^+). **5a**: IR 1745 (C=O); NMR 0.74 (s, C(4)CH_3 cis to C_6H_5), 1.13, 1.15, 1.21 (s, 3H each, $3CH_3$), 1.84 (s, CH_2), 3.37 (s, $C\underline{H}C_6H_5$), 6.9–7.4 (m, C_6H_5); mass *m/e* 216 (M^+). **6a**: IR 1665 (C=C); NMR 1.34, 1.46 (s, 6H each, $4CH_3$), 1.84 (s, CH_2), 4.95 (s, =CH), 6.9–7.5 (m, C_6H_5); mass *m/e* 216 (M^+).

7. **3b**: IR 1716 (C=O), 888 ($=CH_2$); NMR 1.66 (br s, $=CCH_3$), 2.0–2.3 (m, $=CCH_2$), 2.3–2.6 (m, $COCH_2$), 3.58 (s, $C\underline{H}_2C_6H_5$), 4.55, 4.63 (m, 1H each, $=CH_2$), 7.0–7.4 (m, C_6H_5); mass *m/e* 188 (M^+). **5b**: mp 79–80 °C; IR 1748 (C=O); NMR 0.70 (s, C(3)CH_3 cis to C_6H_5), 1.20 (s, CH_3), 1.7–2.0, 2.2–2.5 (m, 2H each, $2CH_2$), 3.06 (s, CH), 6.9–7.3 (m, C_6H_5); mass *m/e* 188 (M^+).
8. The remainder consisted of intractable polymeric substances. Such low yield does not disturb the argument described herein, however.
9. R. Noyori, F. Shimizu, K. Fukuta, H. Takaya, and Y. Hayakawa, *J. Am. Chem. Soc.*, **99**, 5196 (1977).
10. If one assumes that **6a** also came from **9U**, the factor may be taken as 12.
11. Cf. R. Huisgen and R. Schug, *J. Am. Chem. Soc.*, **98**, 7819 (1976). **7** (or **8**) and **9U** differ in their geometry (atomic positions).
12. R. Noyori, S. Makino, and H. Takaya, *J. Am. Chem. Soc.*, **93**, 1272 (1971); R. Noyori, Y. Baba, S. Makino, and H. Takaya, *Tetrahedron Lett.*, 1741 (1973); H. Takaya, S. Makino, Y. Hayakawa, and R. Noyori, *J. Am. Chem. Soc.*, in press.
13. Both 1,1,3,3-tetraalkyl-2-oxyallyls and 1,3-dialkylated species cycloadd across 1,3-dienes equally well. However, the reaction of the former with aromatic olefins is much more sluggish than that of the latter.