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REACTIVITY OF DIENETRICARBONYLIRON COMPOUNDS IN FRIEDEL—CRAFTS ACYLATION

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Summary

Relative reactivities for substituted dienetricarbonyliron compounds toward the methyloxocarbonium tetrachloroaluminate ion pair in dichloromethane have been determined by a competition method. Substituent effects are generally small. However, substituted carbons are not attacked themselves, and acyl groups are strongly deactivating. Some diene complexes which give low yields of acylation product react rapidly with the electrophile nevertheless. These data require that formation of the transition state for electrophilic attack causes small decreases in electron density at the diene carbons. Our data along with data from the literature seem most consistent with rate determining electrophilic attack at carbon.

Introduction

Friedel—Crafts acylation of transition metal-complexed dienes and polyenes is, by now, a familiar reaction [1]. Ligands successfully acylated include simple 1,3-dienes [1a-f] cycloheptatriene [1g], cyclooctatetraene [1h], heptafulvenes [1i], an azepine [1j], tetramethylallene [1k], cyclobutadiene [1l], and trimethylenemethane [1m]. The value of metal complexation in these reactions lies not in activation of the polyene but in control of the reaction. In their review of aliphatic acylation, Nenitzescu and Balaban describe no successful acylation of a 1,3-diene [2]. In fact, Friedel—Crafts reagents are excellent catalysts for cationic polymerization of 1,3-dienes [3]. Cyclooctatetraene gives mainly polymer and little or no acyl derivative under Friedel—Crafts conditions

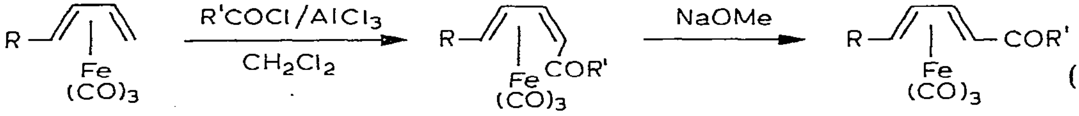

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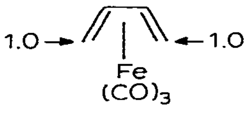
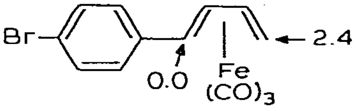
TABLE 1

RELATIVE PARTIAL RATE FACTORS FOR ACETYLATION WITH ACETYL CHLORIDE/ALUMINUM CHLORIDE IN DICHLOROMETHANE AT 25°C [a, b]



(I)



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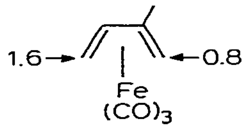

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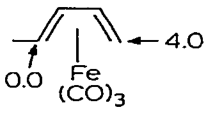

(IV)

[a] 0.1 *M* acetyl chloride/aluminum chloride. Reactants were always at least in five-fold excess. [b] Values are the average of 4—5 determinations. Individual values were within a range of ±5% except for I for which the range was ±9%.

[4]. Cycloheptatriene undergoes either hydride abstraction [5] or addition [6]. Development of the reaction with 1,3-diene complexes has led to stereospecific syntheses of both *syn* and *anti* acylated dienetricarbonyliron compounds (eq. 1) [7], Acylation occurs only at unsubstituted terminal carbons. Oxidation produces the acylated dienes themselves [8], which are inaccessible via direct acylation. We report below a study of relative reactivities of substituted dienetricarbonyliron compounds in Friedel—Crafts acylation [9].

Results

Relative reactivities were determined for 4 tricarbonyliron complexes of simple 1,3-dienes by allowing them to compete with *m*-xylene for a limited amount of acetyl chloride—aluminum chloride complex in dichloromethane. Product ratios were determined by injection of crude product from an aqueous quench directly onto the column of a liquid chromatograph [10]. A check of our method gave a value of 140 for the toluene/benzene reactivity ratio which is close to the values of 128 and 141 observed in 1,2-dichloroethane [11] and carbon disulfide [12], respectively. Our results are expressed in terms of partial rate factors, which represent reactivity of individual carbons [13], and are presented in Table 1. The concentration ratio *m*-xylene/diene complex could be varied from run to run with no change in the measured relative reactivity. No products derived from electrophilic attack at substituted carbons were detected.

This method, being based on analysis of product mixtures, gives accurate results only for compounds which produce acetyl derivatives in high yields. Thus, (1-methoxyl-1,3-butadiene)tricarbonyliron, which is destroyed under acylating conditions cannot be compared to I—IV. [*] Useful qualitative comparisons can be made, however.

Compound I gave no trace of diacylation product in the presence of a large

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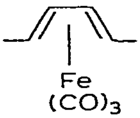
[*] Demethylation of anisoletricarbonylchromium under acylation conditions is a problem [40].

excess of acylating agent, and subjection of the monoacylation product to acylation conditions resulted only in its recovery in high yield. Thus, an acetyl group is highly deactivating. (*trans,trans*-2,4-Hexadiene)tricarbonyliron(V) gave no acyl derivative. Reaction times of 24 h gave only decomposition products and recovered V. The cyclohexadiene derivative, VI, was consumed slowly to give a mixture with weak ketone carbonyl absorption in the infrared. Qualitatively VI is more reactive than V. Under competitive conditions benzene was acylated in the presence of V and VI. Thus, both are less reactive than benzene.



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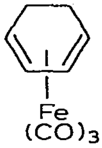
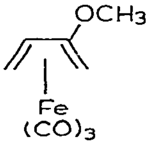


(VI)

Complex VII gives only a 38% yield (isolated) of its acyl derivative, while VIII gives a product mixture with only weak ketone carbonyl absorption in the infrared. VIII does give a formyl derivative in 27% yield on treatment with $Cl_2CHOCH_3/TiCl_4$ [7,14]. Nevertheless, the presence of VII or VIII in solution drastically reduced acetylation of *m*-xylene in competition experiments. The results of these experiments were used to estimate relative reactivities for VII and VIII as 2 times and 2—3 times that of IV, respectively. These observations can be summarized in the following list of relative reactivities: *trans*-1-acetylbutadienetricarbonyliron < V < VI < I < 1-(*p*-acetylphenyl)butadienetricarbonyliron < II < III < IV < VII < VIII.



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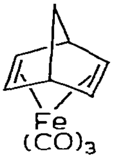


(VIII)

Discussion

Table 2 shows that the reactivity of dienetricarbonyliron complexes is only modestly larger than that of dialkylbenzenes and confirms the observation of Greaves, Knox, and Pauson that I is much less reactive than ferrocene [1b]. Whether complexation to a tricarbonyliron fragment activates or deactivates a diene is not clear. Birch and Pearson accurately described the $Fe(CO)_3$ in reaction 2 as a protecting group. Using the linear free energy relationship developed

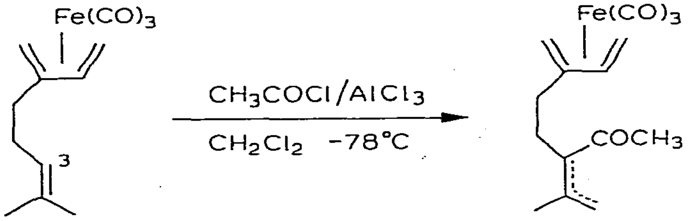
 (2)

TABLE 2

ACETYLATION RATES RELATIVE TO BENZENE IN ACETYL CHLORIDE/ALUMINUM CHLORIDE/DICHLOROMETHANE AT 25°C.

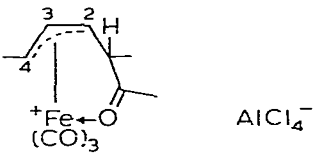
Compound	k_{rel}
Benzene	1.0
Toluene	140
Acetylferrocene [a]	190
m-Xylene	645
ButadieneFe(CO)$_3$ (I)	3850
BromophenylbutadieneFe(CO)$_3$ (II)	4700
2-MethylbutadieneFe(CO)$_3$ (III)	4770
1-MethylbutadieneFe(CO)$_3$ (IV)	7380
1-PhenylbutadieneFe(CO)$_3$ [b]	ca. 1.2×10^5
Anisole [c]	2.9×10^5
Ferrocene [a]	3.3×10^6

[a] At 0°C [41]. [b] *para*-Acetylation only, value approximately ±25%. [c] In 1,2-dichloroethane at 25°C [42].

by Tidwell to describe reactivity of alkenes and dienes in acid catalyzed hydra- [15], we estimate that a 1,1-disubstituted ethylene should be more reactive than a 2-alkyl butadiene by a factor of 70. Thus, initial acylation of uncomplexed triene would probably also occur at C_3, unless steric factors intervened. The reaction in eq. 2 does rule out strong activation of the diene by tricarbonyliron.

Rapid *para* acylation of (1-phenylbutadiene)tricarbonyliron, first reported by Pettit et al., [16], shows that the 1-dienyltricarbonyliron group acts as a powerful activating group in Friedel—Crafts acylation of benzene. This acylation, in contrast to diene acylation, does not proceed via an allyltricarbonyliron cation intermediate. In our experiments the reactivity of (1-phenylbutadiene)tricarbonyliron and anisole appeared equal. Thus, our rough estimate for the former (Table 2) may be low by a factor of 2 to 3.

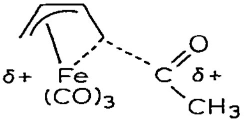
Of the substituent effects determined, only two are large. A 1-acyl substituent completely suppresses further acylation of the diene complex just as it does in benzene derivatives. Alkyl substituents also greatly reduce reactivity at the substituted carbon. Substituted carbons are attacked, albeit at relatively low rates. Gubin et al. [1e] have reported acylation of VI in refluxing methylene chloride, and Greaves et al. [17] have isolated and determined the crystal structure of the σ complex formed by *endo* attack of methyloxocarbonium ion on V (IX). Our observation that V was consumed but no acyl derivative was produced under Friedel—Crafts conditions suggests that the intermediate IX does not produce a significant yield of acyl derivative on hydrolysis. This in turn raises the possibility that compounds like II and IV may also be attacked at their substituted carbons to give intermediates which do not hydrolyze to acyl



(IX)

derivatives. However, the high yields of 4-acyl derivatives from II and IV (84 and 97% isolated) [7] require that this be a minor reaction pathway if it occurs at all.

The other substituent effects are small. The methyl group in toluene activates the *para* position for acetylation by a factor of 770 [11], while the methyl in IV activates C(4) by a factor of only 4. Tidwell et al. [15a] have recently studied substituent effects in acid catalyzed hydration of dienes in aqueous solution at 25°C. The methyl in 2-methyl-1,2-butadiene activates C(1) by a factor of ca. 10^3. In contrast, the methyl in III causes only modest deactivation of C(1) and activation of C(4). Introduction of a 2-methoxy group (VII) causes only a small increase in the acetylation rate in contrast to a hydration rate increase of 10^8 caused by the same change in uncomplexed butadiene [15a]. These small substituent effects find a parallel in acylation of other organometallic π complexes. Those in ferrocenes are slightly larger [18], those in cyclobutadiene-tricarbonylirons are similar [19], and those in η^6-arenetricarbonylchromiums are even smaller [20]. Most of the positive charge in the transition state for electrophilic attack on dienetricarbonyliron compounds must reside on the tricarbonyliron group (X). Further, the lack of significant directive effects (i.e., regioselectivity) in acylation of III and of (η^4-alkylcyclobutadiene)tricarbonyliron compounds, which give 2- and 3-acetyl derivatives in a 1/2 ratio [19], preclude significant



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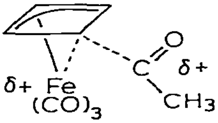
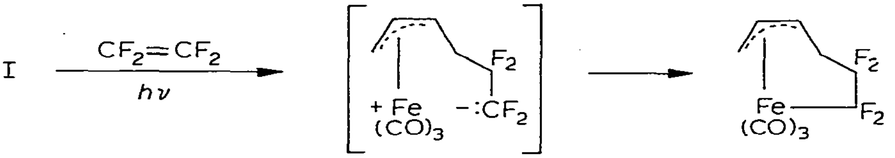


(XI)

charge alternation along the incipient η^3-allyl unit (X and XI) [19]. The related (dienyl)tricarbonyliron cations have a similar charge distribution [21]. This stands in sharp contrast to uncomplexed allyl cations which exhibit strong charge alternation [22].

Green and his coworkers have noted that substituent effects in I, III and IV for photoaddition of tetrafluoroethylene (eq. 3) are strikingly similar to those in Table 1 [23]. A difference is that VI exhibits a reactivity toward tetrafluoroethylene which is comparable to that of I, III and IV. They have proposed a

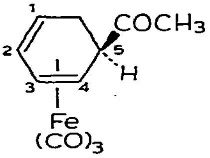


(XII)

(3)

mechanism which involves electrophilic attack of tetrafluoroethylene on a η^2-diene photoproduct to give intermediate XII [23,24]. A number of closely related reactions of diene and polyene tricarbonyliron complexes have been reported [25].

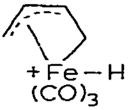
From the electronic viewpoint electrophillic attack is expected to occur in the *endo* sense owing to the high electron density in the region between ligand and metal. In most cases related closely to acylation of complexed dienes this appears to be the case. Cyclohexadiene complexes of iron [26] and rhodium [27] undergo stereospecific *endo* protonation. Cases in which *exo* protonation has been observed all involve polyene complexes, and in some cases protonation of uncomplexed carbons is involved [1g,28]. Tetrafluoroethylene gives the *endo* adduct when it reacts with VI [23]. *Endo* acylation of V has been demonstrated unambiguously by identification of intermediate IX [17]. However, VI gives the *exo* 5-acetyl derivative XIII [1e]. XIII might arise by isomerization of



(XIII)

the *endo* isomer in refluxing CH_2Cl_2, however. Isolation of some 2-acetyl derivative from this reaction [1e] suggests that some isomerization of the initial acylation products is occurring.

The likelihood of preferential *endo* attack raises the possibility that the small substituent effects in Table 1 are the result of rate determining attack at iron, not carbon. The most thoroughly studied reaction of an electrophile with dienetricarbonyliron compounds is the protonation reaction [28,29]. Addition of HX (X = halogen, trifluoroacetate, fluorosulfonate, 1 equivalent) gives carbon-protonated neutral HX adducts. Under conditions of higher acidity, excess FSO_3H or FSO_3H/SbF_5, so-called σ—π cations (XIV) are formed. Simple iron-protonated intermediates (XV) have never been identified. The extant data do



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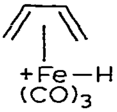

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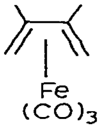

(XVI)

not distinguish between initial iron and carbon protonation. The very low relative reactivity of the bis-terminally-substituted diene complexes V and VI is in better accord with rate determining attack at carbon. The normal reactivity of XVI [1c,e] demonstrates that this is a site-specific effect and is not caused simply by an increase in diene size. We conclude that transition state X for the rate determining step is in best accord with current knowledge of complexed diene acylation and related reactions.

Experimental

General

IR spectra were recorded on a Beckman IR-10 spectrophotometer and were calibrated with the 1601 cm^{-1} polystyrene band. NMR spectra were recorded on Varian Associates A-60 and Perkin—Elmer R-12 spectrometers, and chemical shifts were measured relative to internal tetramethylsilane. Complex V was prepared in 60% yield by $LiAlH_4/AlCl_3$ reduction of (*trans,trans*-sorbaldehyde)tricarbonyliron using the procedure we described previously [7]. Complex VI was prepared according to the method of Pauson [30] and VIII according to the method of Pettit [31]. Preparation of VII is described in ref. 7. Preparations for I, III, IV represent improvements of previously published methods and are described below, as is the preparation of the new compound II.

(1,3-Butadiene)tricarbonyliron (I) *

A 250-ml round-bottom Pyrex flask was equipped with a fritted gas injection tube, thermometer, magnetic stirrer, and a 1 l dry ice/acetone condenser and charged with 200 ml (1.49 mol) of iron pentacarbonyl. The system was swept with nitrogen followed by sufficient 1,3-butadiene to lower the temperature of the liquid phase to +10° C. This mixture was irradiated with a 275-W General Electric sunlamp for 48 h. The temperature was maintained between 50 and 70° C for 16.5 h and between 80 and 100° C for the last 31.5 h by periodic injection of butadiene. After filtration, unreacted iron pentacarbonyl was distilled off at 25° C/12 mmHg. Subsequent distillation at 0.3 mm gave 33.1 g (44% based on net $Fe(CO)_5$ consumed) of I as an orange oil, b.p. 27—29° C/0.3 mmHg. IR and NMR spectra were identical to those reported [33—36].

(trans-1,3-Pentadiene)tricarbonyliron (IV)

trans-1,3-Pentadiene (66.0 ml, 0.662 mol) and iron pentacarbonyl (150 ml, 1.11 mol) in 25 ml benzene were irradiated through a Pyrex flask for 38 h using the 275-W sunlamp. Work-up as described above for I gave 85 g (65%) of an orange oil, b.p. 69—71° C/12 mmHg. IR (film): 2038, 1964 cm^{-1} ($C\equiv O$); NMR ($CDCl_3$): τ 9.78 (q, 1, $J_{1\,anti,\,1\,syn} = 2$ Hz, $J_{1\,anti,2} = 8$ Hz, $H_{1\,anti}$), 8.75—9.10 (m, 1, H_4), 8.60 (d, 3, $J_{4,CH_3} = 5$ Hz, CH_3), 8.25—8.50 (m, 1, H_{1syn}), 4.70—5.00 ppm (m, 2, H_2 and H_3). Chemical shift data only were reported by Emerson et al. [34].

(trans-1-(p-Bromophenyl)-1,3-butadiene)tricarbonyliron (II)

A mixture of triiron dodecacarbonyl (7.59 g, 15.1 mmol) and *trans*-1-(*p*-bromophenyl)-1,3-butadiene (10.68 g, 51 mmol) in 65 ml anhydrous tetrahydrofuran was stirred and heated at reflux under nitrogen for 10 h. Filtration and evaporation of solvent left a dark residue which was dissolved in hexane and passed through a short column of alumina to remove polar impurities. Evaporation of the hexane left an orange solid which was purified by 3 recrystallizations from pentane at —78° C to give 4.62 g (29%) of a yellow powder, m.p. 90—91° C: IR (CCl_4): 2050, 1980 ($C\equiv O$). 1470—1498, 1077, 1007 cm^{-1}; NMR ($CDCl_3$): τ 9.40 (q, 1, $J_{4\,anti,\,4\,syn} = 2.5$ Hz, $J_{4\,anti,\,3} = 9$ Hz, $H_{4\,anti}$), 8.0—8.3 (m, 2, H_1 and $H_{4\,syn}$), 4.65 (m, 1, H_3), 4.17 ppm (q, 1, $J_{1,3} = 8.5$ Hz, $J_{2,3} = 5$ Hz, H_2).

Elemental analysis consistently gave high values for C and H, e.g., found: C, 46.19; H, 2.91; calcd. for $C_{13}H_9BrFeO_3$: C, 44.74; H, 2.60%. Accordingly, the complex was also characterized as its acetyl derivatives which gave satisfactory elemental analyses. These have been described previously [7].

(2-Methyl-1,3-butadiene)tricarbonyliron (III)

III was prepared by irradiation of a solution of isoprene (66.0 ml, 0.662 mol)

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* A similar photochemical preparation has been described in ref. 32.

and iron pentacarbonyl (150 ml, 1.11 mol) in 50 ml benzene using the procedure described for IV above. The product was obtained as 39.5 g (29%) of a yellow oil, b.p. 33—35° C (0.8 mmHg): IR (film): 2045, 1965 cm^{-1}; NMR ($CDCl_3$): τ 10.0 (q, 1, $J_{4\,anti,4\,syn}$ = 2 Hz, $J_{3,4\,anti}$ = 9 Hz, $H_{4\,anti}$), 9.72 (d, 1, $J_{1\,anti,1\,syn}$ = 2 Hz, $H_{1\,anti}$), 8.40 (q, 1, $J_{4\,syn,4\,anti}$ = 2 Hz, $J_{3,4\,syn}$ = 7 Hz, $H_{4\,syn}$), 8.22 (t, 1, $J_{1\,syn,1\,anti} = J_{1,3}$ = 2 Hz, $H_{1\,syn}$), 7.84 (s, 3, CH_3), 4.75 ppm (q, 1, $J_{3,4\,syn}$ = 7 Hz, $J_{3,4\,anti}$ = 9 Hz). These spectral data are in full accord with structure III which was assigned by King et al. [34].

Competitive acylations

Dichloromethane was purified by treating 1 l with 20 g anhydrous aluminum chloride, stirring for 12 h, and quenching with water. The layers were separated, and the dichloromethane was washed several times with water. After drying ($CaCl_2$), distillation from calcium hydride gave a center cut, b.p. 40—41° C.

A stock solution of the Perrier reagent [37] was prepared by introduction of 30 ml dry dichloromethane into a side-arm flask connected to a source of flowing dry nitrogen. After cooling to 0° C in an ice bath, freshly distilled acetyl chloride (0.25 ml, 3.5 mmol) was added from a syringe, followed by 0.40 g (3.0 mmol) of freshly sublimed, pulverized aluminum chloride. After stirring for 1 h, the solution was allowed to warm to 25° C giving a 0.1 *M* solution containing a 15% excess of acetyl chloride. A blanket of dry nitrogen was maintained over the solution during all the above operations.

Competition experiments were performed as follows. Diene complex and *m*-xylene were weighed into dry volumetric flasks, and dry dichloromethane was added to bring the volume to 10.0 ml. Aliquots of 1.0 ml were removed using volumetric pipettes and were delivered to dry 4-ml test tubes. Aliquots of 0.3 ml stock Perrier solution were added to these test tubes which were immediately stoppered, shaken, and introduced into a bath maintained at 25 ± 0.5° C (ambient temperature was 25° C during these experiments). A blanket of dry nitrogen was maintained over the solutions during the above operations. Samples were maintained at 25° C with periodic shaking for 10.0 ± 0.1 min, and then were quenched by rapid injection of 1.5 ml 5% aqueous potassium carbonate. Quenched samples were shaken for 1 min and allowed to stand an additional 5 min. The aqueous layer was removed using a Pasteur pipette, and the organic layer was washed with two 1.5 ml portions of water. Ca. 90% of the dichloromethane was removed in a stream of nitrogen, and the residue was diluted with methanol to 10 ml.

One microliter samples were injected into a liquid chromatograph for analysis. Details of the separation have been described elsewhere [10]. Peaks were monitored using a UV detector operating at 254 nm. Peak areas were determined using a Disc integrator and were normalized by division by molar absorptivity values at 254 nm. These values were determined in the LC moving phase, 20% aqueous methanol (v/v) for aliphatic dienones and 40% aqueous methanol (v/v) for aromatic dienones, using Cary-14 and Beckman-DU (equipped with a Gilford detector) spectrometers. * Relative rates were calculated using eq. 4 which includes a correction for the change in starting material ratio during the

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* Individual values are reported in ref. 39.

course of the reaction [38]. Quantities in eq. 4 are: P, initial concentration of the Perrier complex; A_0, initial concentration of component A; B_0, initial concentration of component B; and R, the final ratio acylation products of A/acylation products of B. At least 4 runs were made for each competition reaction. For further details see ref. 39.

$$k_{\mathrm{rel}} = \log\left[1 - \frac{P}{A_0}\frac{R}{1+R}\right] \bigg/ \log\left[1 - \frac{P}{B_0}\frac{R}{1+R}\right] \qquad (4)$$

Estimates of relative reactivities involving complexes such as V—VIII which did not produce acyl products in high yield were made using the competition and LC analysis described above.

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