Electronic Effects in Migratory Groups. [1,4]- versus [1,2]-Rearrangement in Rhodium Carbenoid Generated Bicyclic Oxonium Ylides

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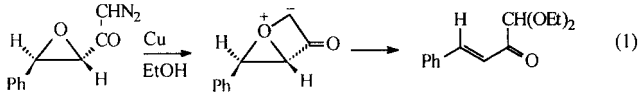
Received April 25, 2001

The variety of α-diazo *β*-keto esters **(3a**−**f**, **8a**−**f)** with varying substituents (ED/EW) on the phenyl ring of the *O*-benzyl group were prepared. The rhodium(II) acetate catalyzed decomposition of diazo compounds in benzene reflux conditions. The ratio of 1,4 versus 1,2 migration product was determined. It was found that an increase in electron density on the benzylic carbon of the migrating group prefers 1,4 migration products **(4**, **9**) while a decrease in electron density leads to a preponderance of 1,2 migration products **(5**, **10**). The results obtained were correlated to the mechanistic aspect of the product selectivity. The intermediacy of the intramolecular oxonium ylide formation was demonstrated by crossover experiments. The preference for the formation of 2,3 sigmatropic rearrangement product over 1,2 and 1,4 was demonstrated by performing the reaction with α-diazo *β*-keto esters **(13a**, **13b)** with *O*-allyl and *O*-propargyl at C3. The effect of solvent, temperature, and mole percentage of rhodium(II) acetate was also studied.

The intramolecular generation of oxonium ylides by rhodium(II)-catalyzed decomposition of α-diazo carbonyl compounds and subsequent transformation to diverse products has received great attention in the past decade.[1] In general, the oxonium ylides undergo three major reaction pathways, which include (a) the *β*-hydride elimination,[2] (b) the [1,2]-migration (Steven's rearrangement),[3] and (c) the [2,3]-sigmatropic rearrangement.[4] Thijs and Zwanenburg had first proposed an intramolecular formation of four-membered oxonium ylide, in the reaction of α,*β*-epoxy diazomethyl ketones with activated copper powder in hydroxylic solvents, to produce alkene oxoacetals (eq 1).[5] In 1984, Doyle and co-workers reported



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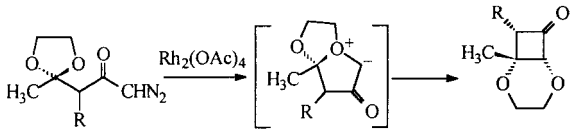
the formation of product in the reaction of acrolein dimethyl acetal and ethyl diazoacetate via the intermediacy of the oxonium ylide.[6] Soon after, Roskamp and Johnson had noticed the formation of [1,2]-rearrangement product in the intramolecularly generated oxonium ylide from α-diazo ketone bearing a cyclic acetal (eq 2).[3c]



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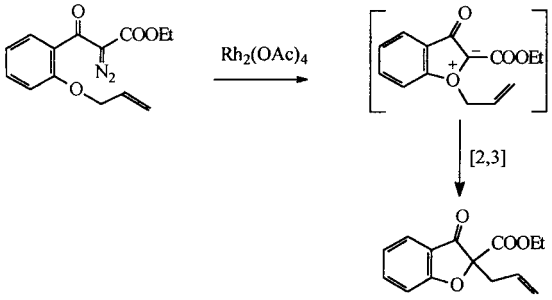
Subsequently, the intramolecular generation of allylic oxonium ylides and their [2,3]-sigmatropic rearrangements in the synthesis of useful oxygen heterocycles gained a lot of interest (eq 3).[4] Besides these usual



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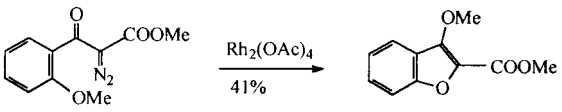
pathways, Pirrung and co-workers in 1991 first observed an example of [1,4]-migration in the rhodium(II)-catalyzed decomposition of an α-diazo-*β*-keto ester (eq 4).[7] The



(4)

second report by West and co-workers described the isolation of the [1,4]-migration product, *albeit* in very low

(1) For general reviews of rhodium-carbenoids, see: (a) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765. (b) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385. (c) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (d) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223. (e) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (f) Sulikowski, G. A.; Cha, K. L.; Sulikowski, M. M. *Tetrahedron*: *Asymmetry* **1998**, *9*, 3145.

(2) Bien, S.; Gillon, A.; Kohen, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 489.

(3) (a) Brogan, J. B.; Bauer, C. B.; Rogers, R. D.; Zercher, C. K. *Tetrahedron Lett.* **1996**, *37*, 5053. (b) Doyle, M. P.; Ene, D. G.; Forbes, D. C.; Tedro, J. S. *Tetrahedron Lett.* **1997**, *38*, 4367. (c) Roskamp, E. J.; Johnson, C. R. *J. Am. Chem. Soc.* **1986**, *108*, 6062.

(4) (a) Pirrung, M. C.; Werner, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 6060. (b) Clark, J. S. *Tetrahedron Lett.* **1992**, *33*, 6193. (c) Doyle, M. P.; Bagheri, V.; Harn, N. K. *Tetrahedron Lett.* **1988**, *29*, 5119.

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(6) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; Van Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917.

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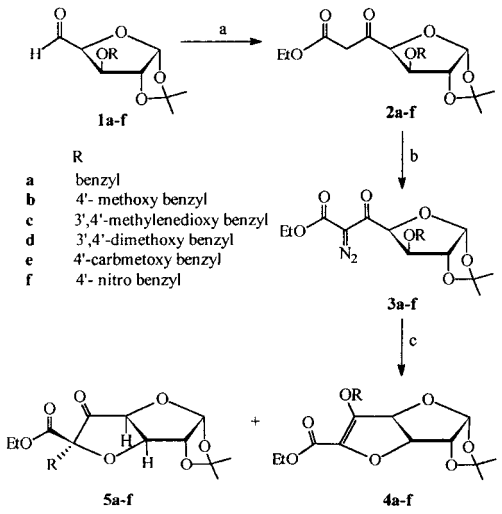
10.1021/jo010431f CCC: $20.00
Published on Web 08/29/2001

Scheme 1[a]



[a] Key: (a) $BF_3{\cdot}OEt_2$, EDA, CH_2Cl_2, 0 °C, 3 h; (b) MsN_3, CH_3CN, 30 °C, 3 h; (c) $Rh_2O(Ac)_4$, benzene, reflux, 10−30 min.

yield, in the Cu(II) carbenoid-derived oxonium ylides.[8] The same reaction, however, failed to give the [1,4]-migration product in the presence of rhodium(II) acetate. Recently, we have substantiated this uncommon behavior and demonstrated that the formation of the [1,4]-migration product, via the intermediacy of oxonium ylide, is also a prominent process.[9] Our results showed that the decomposition of the sugar derived α-diazo-*β*-keto ester **3a**, catalyzed with rhodium(II) acetate, gave the [1,4]-migrated product **4a** in major amount (62%) in competition with the [1,2]-rearrangement product **5a** (38%). In the case of **3b**, in which the migratory −*O*Bn group is replaced with −*O*PMB, the formation of [1,4]-migration product **4b** was the only isolated product in 80% yield (Scheme 1). This precedent provided us a useful system to study the intramolecular competition between the formation of [1,4]- and [1,2]-migration products, as a function of migratory aptitudes of the migrating group, in the rhodium carbenoid generated bicyclic oxonium ylides.

Many competitive studies related to the product selectivity in rhodium carbenoid reactions, leading to either C−H insertion or rearrangements, are reported. These are mainly classified in two types. The first and the most commonly used methodology is catalyst specific in which product selectivity is dependent on the electrophilic nature of the rhodium(II) catalyst (by variation of ligands on rhodium).[10] The chiral rhodium catalysts are known to give chemo- and stereoselectivity in product formation.[11] The second type of studies are substrate specific. A few examples of this type are known wherein six-membered versus five-membered oxonium ylide formation (which is dependent on which diastereotopic oxygen out of the two possible oxygen atoms is involved in the oxonium ylide formation) decides the product distribution.[12] The third factor that controls the product formation is the reaction conditions (i.e., solvent, temperature, and molar ratio of catalyst to substrate).[13] Our present study is related to the specificity due to substrate. In this aspect, we changed the migratory aptitude of the migrating group (by incorporating electron-donating and electron-withdrawing groups in the phenyl ring of the benzyl group) that is bonded to the oxygen of an oxonium ylide generated from Rh(II)-catalyzed decomposition of α-diazo *β*-keto ester. We report here the general trend that an increase in the electron density on the benzylic carbon of the migratory group results in the preferential [1,4]-migration pathway while a decrease in the electron density leads to the preponderance of the [1,2]-migration product. The results thus obtained are correlated to the mechanistic aspects in the formation of the [1,4]- and [1,2]-migrated product.

Table 1. Electronic Effect of Substituent on the Formation of 1,4 and 1,2 Migration Products

entry	diazo compd	time (min)	products 1,4	products 1,2	ratio 1,4:1,2	combined yield[a](%)
1	**3a**	10	**4a**	**5a**	62:38	77
2	**3b**	30	**4b**	**5b**	100:0	75
3	**3c**	30	**4c**	**5c**	100:0	75
4	**3d**	30	**4d**	**5d**	100:0	76
5	**3e**	10	**4e**	**5e**	38:62	81
6	**3f**	10	**4f**	**5f**	32:68	82
7	**8a**	30	**9a**	**10a**	100:0	76
8	**8b**	30	**9b**	**10b**	100:0	73
9	**8c**	30	**9c**	**10c**	100:0	76
10	**8d**	10	**9d**	**10d**	58:42	78
11	**8e**	10	**9e**	**10e**	60:40	76
12	**8f**	30	**9f**	**10f**	100:0	65

[a] Isolated yields after column chromatography.

Results and Discussion

The required D-glucose-derived *β*-keto esters, with varying substituents on the phenyl ring of the benzyl group at C3 oxygen, were prepared as per the procedure reported earlier by us.[14] Thus, the individual reactions of 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdoses **1a**−**f** with ethyl diazoacetate (EDA) in the presence of $BF_3{\cdot}OEt_2$ in dichloromethane at 0 °C (for electron-donating substituents the reactions were performed at −50 °C) afforded the corresponding sugar *β*-keto esters **2a**−**f**. The diazo transfer with mesyl azide completed the transformation of *β*-keto esters **2a**−**f** to the corresponding α-diazo *β*-keto esters **3a**−**f** in good yields. The reactions of **3a**−**f** with $Rh_2(OAc)_4$ (2 mol %) were conducted under benzene reflux conditions until the starting material was consumed as indicated by TLC (Scheme 1). The reaction mixture was directly chromatographed, and the corresponding 1,4-migrated products **4a**−**f** and 1,2-migrated products **5a**,**e**,**f** were isolated in good yields (70−82%).[15] The results are summarized in Table 1. We have also tested the generality of this reaction with aromatic substrates. In this case, reaction of the aromatic aldehyde derivatives **6a**−**f** using EDA and $BF_3{\cdot}OEt_2$ afforded poor yields of *β*-keto esters.

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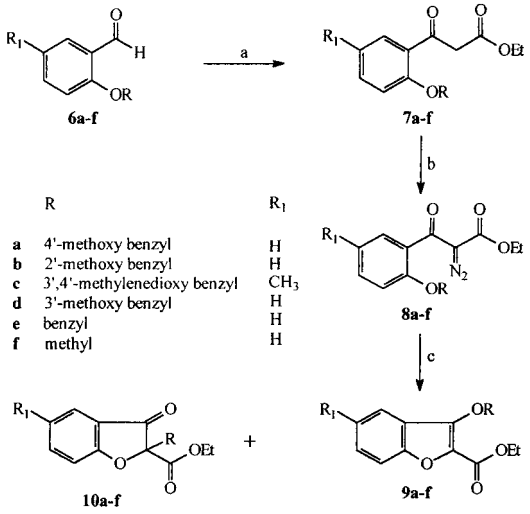
(12) Zercher, C. K.; Brogan, J. B.; Bauer, C. B.; Rogers, R. D. *Tetrahedron Lett.* **1996**, *37*, 5053.
(13) Wee, A. G. H.; Liu, B.; McLeod, D. D. *J. Org. Chem.* **1998**, *63*, 4218.
(14) Dhavale, D. D.; Bhujbal, N. N.; Joshi, P.; Desai, S. G. *Carbohydr. Res.* **1994**, *263*, 303.
(15) No product corresponding to an alternative pathway such as C−H insertion or Buchner reaction (possible with the in situ generated rhodium carbenoid) was isolated.

Scheme 2[a]



[a] Key: (a) Activated Al_2O_3, EDA, 25 °C, 3 h; (b) MsN_3, CH_3CN, 30 °C, 3 h; (c) $Rh_2O(Ac)_4$, benzene, reflux, 10−30 min.

However, the use of EDA and activated alumina under solvent free conditions as reported earlier by us[16] gave the corresponding *β*-keto esters **7a**−**f** in good yields.[17] The reaction of **7a**−**f** with mesyl azide gave α-diazo *β*-keto esters **8a**−**f**, respectively (Scheme 2). Treatment of **8a**−**e** with $Rh_2(OAc)_4$ (2 mol %) under benzene reflux conditions gave identical results, and corresponding 1,4-migrated products **9a**−**e** and 1,2 migrated products **10d**,**e** were isolated in 70−80% yields (Table 1).[18]

The 1,4- and 1,2-migrated products (**4**, **9** and **5**, **10)** were well characterized by spectroscopic and analytical data. The characteristic features for 1,2-migrated products were as follows. The IR spectra showed two carbonyl frequencies at 1779 and 1744 cm^{-1} indicating the presence of a five-membered ring ketone (furan-3-one) and the ester carbonyl group, respectively. The ^1H NMR spectra showed an AB quartet at δ ~3.26 (J = 14.0 Hz) indicating the presence of a $-CCH_2Ph$ group instead of $-OCH_2Ph$ functionality. The ^{13}C NMR spectrum showed a ketone carbonyl at δ_C ~202.3 and ester carbonyl at δ_C ~166.9. The assignments of the 1,4-migration products were also made by spectral studies. The IR spectra showed a carbonyl stretching frequency at 1714 cm^{-1} corresponding to α,*β*-unsaturated ester functionality. In the ^1H NMR spectrum, the $-OCH_2Ph$ group displayed a signal at δ ~5.16 (AB quartet with J = 12.1 Hz or singlet) and ^{13}C NMR showed only one ester carbonyl at δ_C ~160.1 and two olefin carbons. The structure of **4a** was further confirmed by ^{13}C DEPT, 2D NMR experiments such as HETCORR, COSY, and elemental analysis data.[9]

Examination of the results indicated that the rhodium(II)-catalyzed reactions of α-diazo *β*-keto esters **3b**−**d** and **8a**−**c**,**f** (with electron-donating substituents) afforded respective 1,4-migrated products **4b**−**d** and **9a**−**c**,**f** as the only isolable compounds in greater than 70% yields (Table 1, entries 2−4, 7−9).[19] Conversely, the reverse trend was noticed in the case of substrates **3e**,**f** (with electron-withdrawing substituents) wherein the 1,4-migrated products **4e**,**f** were obtained in minor amounts while the 1,2-migrated products **5e**,**f** were the major ones (Table 1, entries 5 and 6). However, in the case of **3a** and **8e** (unsubstituted benzyl group), the predominant formation of 1,4-migrated product (~60%) over 1,2-migrated product (~40%) was noticed (Table 1, entries 1 and 11). A similar trend was noticed for **8d** (3′-methoxybenzyl-substituted), although there is an overall increase in the electron density in the phenyl group (Table 1, entry 10). To understand the effect of the reaction conditions[13] (solvent, temperature, and molar ratio) on the product selectivity, we have performed the reactions with the model substrate **3a** (Table 2). The reaction of **3a** with rhodium acetate (2 mol %) in dichloromethane at room temperature or under reflux conditions afforded a complex mixture of products (Table 2, entries 1 and 2) while in benzene at room temperature it was noticed to be very sluggish and even after 36 h nearly quantitative amounts of starting materials were recovered (Table 2, entry 3). The optimum conditions (benzene reflux, 10 min, Table 2, entry 4) afforded the 1,4-migrated and 1,2-migrated products **4a** and **5a**, respectively, in a ratio of 62:38 in 77% yields. An increase in the amount of $Rh_2(OAc)_4$ (5 mol %) had no significant effect (Table 2, entry 5). To test whether even higher temperature would be advantageous, the reaction was performed in refluxing toluene. However, this did not alter the course of the reaction (Table 2, entry 6).

Table 2. Effect of Reaction Conditions on the Reaction of 3a with Rhodium Acetate

entry	$Rh_2(OAc)_4$ (mol %)	solvent	T (°C)	time	ratio 1,4:1,2	yield[a] (%)
1	2	CH_2Cl_2	25	1 h		
2	2	CH_2Cl_2	40	1 h		
3	2	C_6H_6	25	36 h		90[b]
4	2	C_6H_6	80	10 min	62:38	77
5	5	C_6H_6	80	10 min	64:36	78
6	2	$C_6H_5CH_3$	110	10 min	60:40	78

[a] Isolated yields after column chromatography. [b] Yield of recovered compound.

Next, the competitive reaction pathway between [2,3]-sigmatropic rearrangement and [1,4]- or [1,2]-rearrangement was studied. To explore such a possibility, D-glucose-derived 3-*O*-allyl-*β*-keto ester **12a** and 3-*O*-propargyl-*β*-keto ester **12b** (obtained from 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdoses **11a** and **11b**) were converted to the corresponding α-diazo-*β*-keto esters **13a** and **13b** in good yields (Scheme 3). The individual reactions of **13a** and **13b** with rhodium(II) acetate (2 mol %) under benzene reflux conditions (10 min) furnished [2,3]-sigmatropic rearrangement products **14a** and **14b**, respectively, in good yields (~75%). This indicated that the in situ generated oxonium ylides have a preference for the symmetry-allowed [2,3]-sigmatropic rearrangement over the [1,2]- and [1,4]-migration products.[20] In view of the fact that in metal carbenoid reactions [2,3]-sigmatropic

(16) Dhavale, D. D.; Patil, P. N.; Mali, R. S. *J. Chem. Soc.*, **1994**, 152.

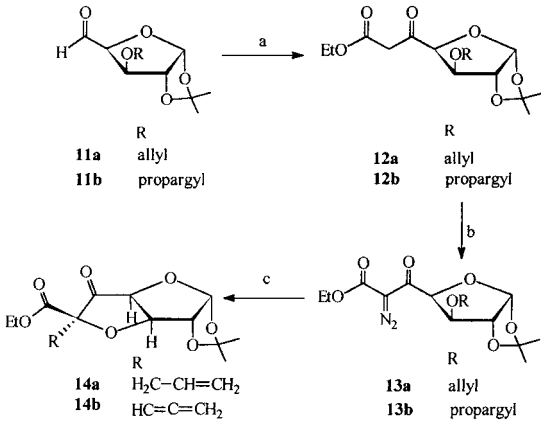
(17) The reactions of 2-*O*-(4′-nitrobenzyl) benzaldehyde and 2-*O*-(4′-carbemethoxybenzyl) benzaldehyde with EDA either in the presence of BF_3-OEt_2 in dichloromethane or activated alumina under solvent free conditions failed to give the corresponding *β*-keto esters under variety of reaction conditions.

(18) We have repeated the reaction of benzenepropanoic acid, 2-*O*-methyl-α-diazo-*β*-oxoethyl ester **(8f),** as reported first by Pirrung et al. (see ref 7). In our hands, the reaction under benzene reflux condition afforded 1,4-migrated product **9f** in 65% yield.

(19) In all these reactions the ^1H and ^{13}C NMR spectrum of the crude mixture showed signals (<5%), which could be assigned to the 1,2-migrated product. However, our attempts to isolate the product in pure form were unsuccessful.

(20) Identical results with aromatic substrates have been reported (see refs 4 and 7).

Scheme 3[a]



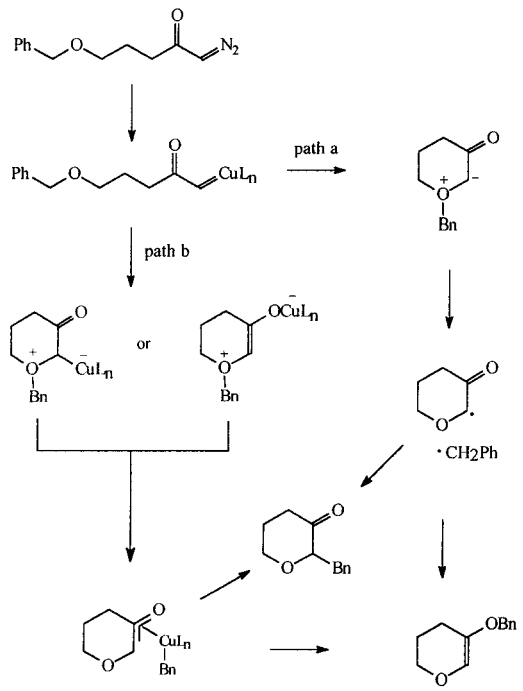
[a] Key: (a) BF_3·OEt_2, EDA, CH_2Cl_2, 0 °C, 3 h; (b) MsN_3, CH_3CN, 30 °C, 3 h; (c) $Rh_2O(Ac)_4$, benzene, reflux, 10 min.

rearrangements have the lower activation energy as compared with other possible pathways,[4] the reaction was performed at lower temperature. The same reaction at 35 °C (lower activation energy) in benzene (3 h) or in dichloromethane (1 h) also afforded **14a** and **14b** in 86% and 78% yields, respectively, indicating that the reaction pathway was indeed a [2,3]-sigmatropic rearrangement.[21]

The absolute configuration at the newly generated stereocenter C6 in 1,2-migrated product **5f** and 2,3-sigmatropic rearrangement product **14a**, was established by NOEDIF experiments. Thus, **5f** showed NOE between the benzylic ($-CH_2$) protons and α-H3, α-H4 as well as two aromatic protons (ortho to the benzylic group) but no NOE with H1 and H2, while for **14a**, an NOE was observed between allylic ($-CH_2$) protons and α-H3, α-H4 as well as three olefinic protons but no NOE was observed with H1 and H2. This indicated that in both products **5f** and **14a** the migrating group comes from the α-face resulting in (*R*) absolute configuration at C6.

Mechanistic Study of the Reaction. Although different mechanisms involved in the rhodium(II) carbenoid-mediated 1,2-rearrangement, [2,3]-sigmatropic rearrangement, and C−H insertion products are well documented in the literature, an explanation for the formation of 1,4-migration product, in the rhodium(II) catalyzed reaction, is lacking. West and co-workers,[8] however, proposed a mechanism in the Cu(II)-catalyzed decomposition of α-diazo ketone for the formation of the [1,2]- and [1,4]-migrated products (Scheme 4). It has been reported that the difference in Rh(II)- and Cu(II)-catalyzed decomposition follow different mechanistic pathways.[1] Therefore, an independent mechanism for the formation of 1,4-migrated product had been proposed by us (Scheme 5).[9,22] We assumed that the metal-bound five-membered oxonium ylide **A** or **B**, generated from substrate **3**, plays an important role in the product selectivity. Examination of models revealed that, in the oxonium ylide **B**, the distance between the migration origin and the terminus is large, thus ruling out its intermediacy in the 1,4-migrated product. On the other hand, we hypothesized a somewhat different type of four-centered oxabicyclo-[3.2.0]heptane transition state (TS) **C**, via the intermediacy of the oxonium ylide **A**, wherein the Rh−C6 bond (metal carbenoid bond) is aligned with the O−CH_2Ar bond. As the reaction proceeds, the migration of the −CH_2Ar group from oxygen to Rh is completed leading to TS **D**. We feel that the TS **D** is the true intermediate in the formation of both the products **4** and **5**. We would like to attribute the differences in the selectivity of the formation of product **4** or **5** to the change in electrophilicity of the Rh complex, in the TS **D**, due to the electronic effects of the substituent in the migrating group. In the case of an electron-rich aromatic ring, due to the stronger back-bonding interaction, the electrophilicity of Rh decreases and the metal carbenoid bond (Rh−C6) becomes weaker as compare to Rh−CH_2Ar bond.[23] Thus, as shown in Scheme 5, free rotation about the metal carbenoid bond (Rh−C6) brings −CH_2Ar (migrating group) close to the C=O group (TS **E**). The rupture of the weak Rh−C6 bond followed by the migration of the benzyl group to oxygen, and exclusion of Rh(II) acetate afforded [1,4]-migrated product **4** by a concerted pathway. However, in the case of electron-poor substituents, due to the increase in electrophilicity of the Rh complex, the bond between Rh−C6 becomes stronger than the Rh−CH_2Ar bond.[23] As a result, the reaction is initiated by cleavage of the weak Rh−CH_2Ar bond followed by formation of a new C−C bond (between benzylic carbon and C6) and cleavage of the Rh−C6 bond with loss of Rh(II) acetate in a three-membered TS **F** by a concerted process to afford 1,2-rearranged product **5**.[24]

Scheme 4



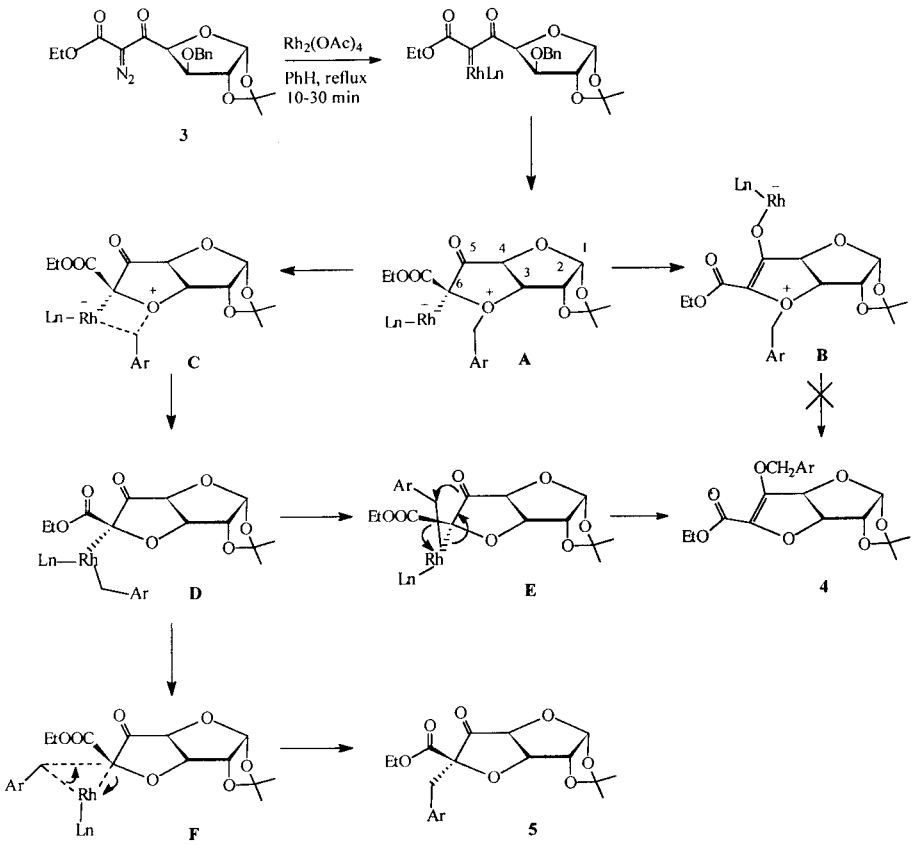
An examination of Table 1 indicated that the reaction time required for the formation of 1,4-migrated product in the electron-rich migratory group is more (30 min) than that required (10 min) for the completion of the

(21) No product corresponding to either [1,4]- or [1,2]-rearrangement was detected in the ^{1}H NMR spectrum of the crude reaction mixture (at reflux or lower temperature).

(22) We are thankful to Prof. Pirrung for helpful discussions.

(23) Pirrung et al. studied the effect of ligands on rhodium in the product selectivity of 1,2 versus C−H insertion. In this study, it has been noticed that in the electron-rich rhodium complexes (e.g., rhodium pivalate) the stronger back-bonding interactions resulted into the shorter Rh−Rh bond and consequently weaker σ bond between metal and carbenoid. A reverse trend had been noticed for electron-poor complexes (e.g., rhodium trifluoro acetate); see ref 10b.

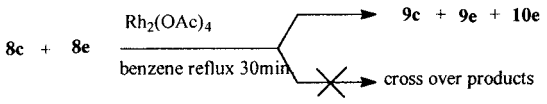
Scheme 5



reactions where the unsubstituted or electron-withdrawing group is present (compare entries 2−4 and 7−9 with all other entries). We would like to attribute this anomaly to the change in Lewis acid character of the Rh complex. The reduction of the Lewis acidity of the complex, for an electron-donating substituent on the phenyl ring, decreases the rate of the formation of products, whereas in the case of electron-withdrawing substituent the increase in Lewis acidity of the complex enhances the rate of formation of the products. This observation was noticed to be parallel with that reported by McKervey and coworkers wherein rhodium (II) carboxylates were found to be more reactive (reaction completed in 10 min) than the Rh(II) MEPY (reaction completed after 3 days even though 10-fold equiv of catalyst was used).[11]

We would like to correlate our observation with the change in charge density at the benzylic carbon. We predict that the partially developed positive charge on the benzylic carbon in the TS **D** stabilized by electron-donating groups on the phenyl ring favors 1,4-migration, whereas the positive charge on the benzylic carbon in the TS **D** destabilized by electron-withdrawing groups on the phenyl ring favors 1,2-rearrangement in the intramolecular pathway. Furthermore, we are correlating the selectivity in product formation with σ_R or a resonance effect based on π-electron bonding and delocalization. Thus, the plot of σ_R (resonance contribution)[25] for the substituent on the phenyl ring of the migratory group against percentage of 1,4- and 1,2-migrated products gives good correlation (Figures 1 and 2). This indicates that resonance contribution due to the substituent on phenyl ring affects the percentage of 1,4- and 1,2-migrated products; i.e., a substituent with positive σ_R favors 1,2-migrated products and a substituent with negative σ_R favors 1,4 migrated products.

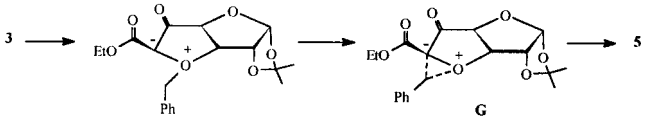
An alternative pathway in which $PhCH_2^+$ (benzyl cation) is dissociated either from the oxonium ylide **B** or from the rhodium(II) species in TS **D** and then attacked by the enolate oxygen of another molecule in an intermolecular fashion could be possible. To probe the inter- or intramolecular pathway of the reaction, we performed a crossover experiment. Thus, the one-pot reaction of mixture of **8c** and **8e** in the presence of Rh(II) acetate (2 mol %) in benzene was performed at reflux temperature for 30 min (eq 5). The reaction after usual workup



(5)

afforded **9c** in 78% and **9e** and **10e** in the ratio 61:39 with overall 80% yield. No crossover product was isolated in the reaction mixture, indicating that the reaction is

(24) Previously, we proposed the mechanism via TS **G** that resembles an oxabicyclo [3.1.0]hexane ring system as shown below; see ref 9.



(25) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1−83, 125−191. This report indicates four parameters: σ_F or field effect, based on charge−charge or dipole−dipole interactions; σ_R or resonance effect, based on π-electron bonding and delocalisation; σ_α or polarizability, based on charge-induced dipoles; σ_x or electronegativity, based on partial ionic character of the σ bond between the substituent and a bonded atom. However, we would like to confine our discussion by correlating σ_R with 1,2- and 1,4-migration product selectivity.

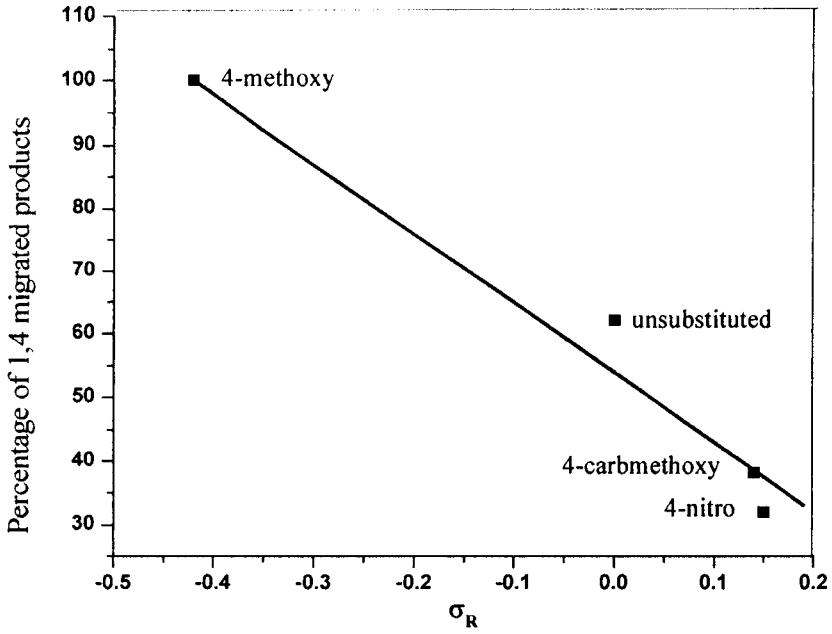


Figure 1. σ_R versus percentage of 1,4-migrated products for the Rh-catalyzed reaction of sugar α-diazo *β*-keto esters.

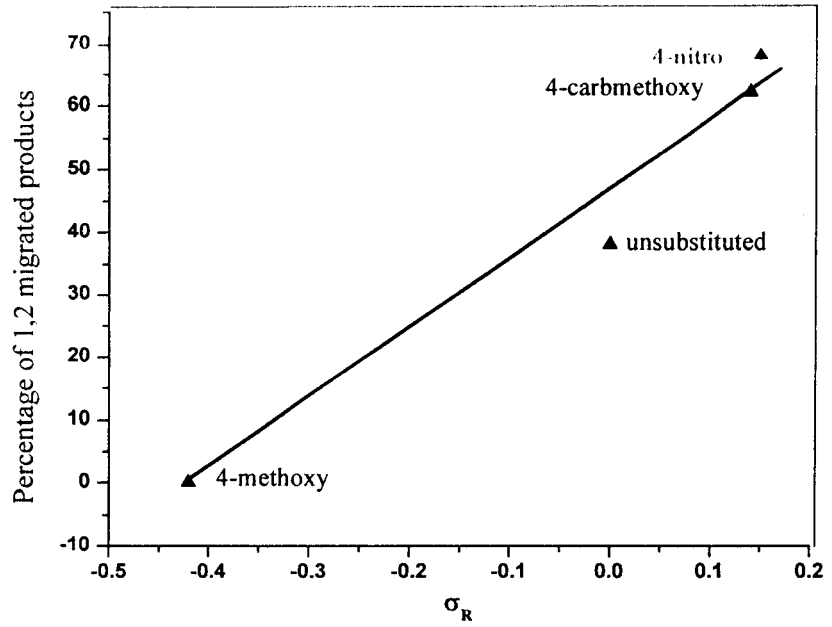
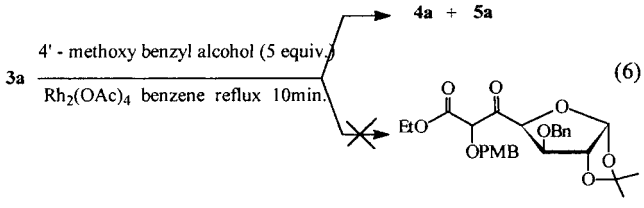


Figure 2. σ_R versus percentage of 1,2-migrated products for the Rh-catalyzed reaction of sugar α-diazo *β*-keto esters.

exclusively intramolecular. To trap the initially formed Rh-carbenoid species and to check the inter- versus intramolecular formation of oxonium ylide, we have performed the rhodium-catalyzed decomposition reaction of **3a** in the presence of *p*-methoxy benzyl alcohol (5 equiv) in benzene at reflux (eq 6). The reaction was completed in 10 min and afforded a mixture of **4a** and **5a** in the ratio 60:40 (combined yield 78%). No product corresponding to −*O*-(*p*-methoxybenzyl) insertion was isolated or detected in the crude ^{1}H NMR spectrum indicating that the intramolecular oxonium ylide formation is a rapid process than the intermolecular C−O insertion.[26] In another attempt, the intermediacy of 1,2-migratory product in the formation of 1,4-migratory product was checked. Thus, reaction of **5a** (1,2-migration product) in the presence of Rh(II) acetate (2 mol %) in benzene at reflux for 8 h resulted in the quantitative recovery of the starting compound. The 1,4-migration product was not detected even in the ^{1}H NMR of the crude product. This experiment thus ruled out the intermediacy of **5a** in the formation of **4a**. Thus, the intramolecular bicyclic oxo-



(26) The decomposition of α-diazo carbonyl compound in the presence of alcohol gives C−O insertion product via the formation of intermolecular oxonium ylide formation; see: Hosten, N. G. C. *Bull. Soc. Chim. Belg.* **1985**, *94*, 183.

nium ylide mechanistic pathway, as depicted in Scheme 5, via the participation of the rhodium metal could be the most probable mechanism for the formation of 1,4-migrated product. However, the role of rhodium catalyst to generate a carbene species followed by 1,4-migration by radical pathway also could not be ruled out.

Conclusion

We have firmly established that the formation of the 1,4-migration product, in the rhodium carbenoid generated bicyclic oxonium ylides, is a prominent process in addition to the usual 1,2-migration or [2,3]-sigmatropic pathways. We have also demonstrated that the migratory aptitude of the migrating group is one of the deciding factors in such competitive processes. The study of effect of different electrophilic rhodium catalysts, by changing the ligands, on the product selectivity and mechanistic aspect involving radical approach is in progress.

Experimental Section

General Methods. Melting points were recorded with a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded with FTIR as a thin film or in Nujol mull or with KBr pellets and are expressed in cm^{-1}. ^1H (300 MHz, 500 MHz) and ^{13}C (75 MHz, 125 MHz) NMR spectra were recorded in $CDCl_3$ as a solvent. Chemical shifts were reported in δ (ppm) with reference to TMS as an internal standard. Elemental analyses were carried out with a C,H analyzer. Optical rotations were measured using a polarimeter at 25 °C. Thin-layer chromatography was performed on precoated plates (0.25 mm, silica gel 60 F_{254}). Flash chromatography was performed on silica gel (200−400 mesh), and column chromatography was carried out with silica gel (100−200 mesh). Whenever required, the reactions were carried out in oven-dried glassware under dry N_2. Acetonitrile, benzene, dichloromethane, and THF, were purified and dried before use. Petroleum ether (PE) that was used is a distillation fraction between 40 and 60 °C. Rhodium acetate dimer was purchased from Fluka; prior to use, $Rh_2(OAc)_4$ was activated by heating at 100 °C under reduced pressure (3 mm of Hg) for 3 h. After workup, the organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated at reduced pressure. The preparation of sugar α-diazo β-keto esters **3a**, **3b**, ans **13a** and reactions of α-diazo β-keto esters **3a**, **3b**, and **13a** with $Rh_2(OAc)_4$ in benzene were reported previously by us.[9,14]

General Procedure for the Preparation of β-Keto Esters (2c−f, 12b). A solution of aldehyde (1 mmol) and ethyl diazoacetate (1.5 mmol) in dry CH_2Cl_2 (15 mL) was cooled under nitrogen atmosphere. A solution of BF_3−etherate (0.3 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise with control of the evolution of N_2 (20 min). The reaction mixture was stirred at cooled temperature until the starting material was consumed and then quenched with a saturated solution of sodium bicarbonate. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (10 mL × 3). The combined organic layer was dried (Na_2SO_4) and evaporated on a rotary evaporator. The residue thus obtained on column chromatography yielded β-keto ester.

Ethyl 6-deoxy-1,2-*O*-isopropylidene-3-*O*-(3′,4′-methylenedioxybenzyl)-α-D-*xylo*-hept-5-ulofuranuronate (2c): reaction performed at −50 °C, for 3 h; white solid; mp 56−58 °C; 74% yield; R_f = 0.41 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = −52.6 (*c* 0.25, $CHCl_3$); IR (Nujol) 1745, 1724 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.77−6.70 (m, 3H), 6.06 (d, *J* = 3.6 Hz, 1H), 5.96 (s, 2H), 4.70 (d, *J* = 3.5 Hz, 1H), 4.56 (d, *J* = 3.6 Hz, 1H), 4.42 (AB quartet, *J* = 11.5 Hz, 2H), 4.26 (d, *J* = 3.5 Hz, 1H), 4.20 (q, *J* = 6.3 Hz, 2H), 3.64 (AB quartet, *J* = 17.1 Hz, 2H), 1.46 (s, 3H), 1.32 (s, 3H), 1.27 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 167.0, 147.8, 147.4, 130.3, 121.5, 112.5, 108.5, 108.0, 106.0, 101.0, 84.9, 83.2, 81.8, 72.5, 61.6, 47.6, 26.9, 26.3, 14.0. Anal. Calcd for $C_{20}H_{24}O_9$: C, 58.82; H, 5.88. Found: C, 58.96; H, 5.76.

Ethyl 6-deoxy-3-*O*-(3′,4′-dimethoxybenzyl)-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-ulofuranuronate (2d): reaction performed at −50 °C, for 3 h; white solid; mp 62−64 °C; 72% yield; R_f = 0.38 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = −56.8 (*c* 0.25, $CHCl_3$); IR (Nujol), 1744, 1726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.81−6.78 (m, 3H), 6.07 (d, *J* = 3.6 Hz, 1H), 4.69 (d, *J* = 3.7 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 4.46 (AB quartet, *J* = 11.1 Hz, 2H), 4.26 (d, *J* = 3.7 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.91(s, 3H), 3.87 (s, 3H), 3.64 (AB quartet, *J* = 16.8 Hz, 2H), 1.46 (s, 3H), 1.32 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 167.0, 149.0, 148.8, 128.9, 120.4, 112.5, 111.0, 110.9, 106.0, 84.9, 82.9, 81.7, 72.3, 68.6, 61.1, 55.8, 47.5, 26.9, 26.3, 14.0. Anal. Calcd for $C_{21}H_{28}O_9$: C, 59.43; H, 6.60. Found: C, 59.23; H, 6.69.

Ethyl 6-deoxy-3-*O*-(4′-carbmetoxybenzyl)-1,2-*O*-isoprpylidene-α-D-*xylo*-hept-5-ulofuranuronate (2e): reaction performed at 0 °C, for 3 h; thick oil; 73% yield; R_f = 0.40 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = −62.2 (*c* 0.25, $CHCl_3$); IR (neat) 1745,1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.05 (d, *J* = 3.5 Hz, 1H), 4.73 (d, *J* = 3.6 Hz, 1H), 4.61 (d, *J* = 3.5 Hz, 1H), 4.48 (AB quartet, *J* = 12.0 Hz, 2H), 4.26 (d, *J* = 3.6 Hz, 1H), 4.20 (q, *J* = 6.2 Hz, 2H), 3.85 (s, 3H), 3.66 (AB quartet, *J* = 18.0 Hz, 2H), 1.45 (s, 3H), 1.32 (s, 3H), 1.25 (t, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.3, 166.6, 166.0, 142.5, 130.4, 128.3, 113.2, 106.2, 85.4, 84.3, 82.6, 72.2, 62.8, 53.4, 48.3, 27.1, 26.8, 14.8. Anal. Calcd for $C_{21}H_{26}O_9$: C, 59.71; H, 6.16. Found: C, 59.82; H, 6.05.

Ethyl 6-deoxy-1,2-*O*-isoprpylidene-3-*O*-(4′-nitrobenzyl)-α-D-*xylo*-hept-5-ulofuranuronate (2f): reaction performed at 0 °C, for 3 h; thick oil; 75% yield; R_f = 0.39 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = -70.6 (*c* 0.25, $CHCl_3$); IR (neat) 1745, 1729, 1522, 1456 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.05 (d, *J* = 3.6 Hz, 1H), 4.71 (d, *J* = 3.3 Hz, 1H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.63 (d, *J* = 3.6 Hz, 1H), 4.57 (d, *J* = 12.2 Hz, 1H), 4.30 (d, *J* = 3.3 Hz, 1H), 4.20 (q, *J* = 6.2 Hz, 2H), 3.66 (AB quartet, *J* = 17.0 Hz, 2H), 1.48 (s, 3H), 1.34 (s, 3H), 1.26 (t, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7, 166.8, 147.5, 143.9, 127.8, 123.6, 112.7, 105.9, 84.8, 84.3, 81.5, 71.2, 61.2, 47.7, 26.8, 26.2, 14.0. Anal. Calcd for $C_{19}H_{23}NO_9$: C, 55.74; H, 5.62. Found: C, 55.70; H, 5.52.

Ethyl 6-deoxy-1,2-*O*-isoprpylidene-3-*O*-(propargyl)-α-D-*xylo*-hept-5-ulofuranuronate (12b): reaction performed at 0 °C, for 3 h; thick oil; 72% yield; R_f = 0.43 (PE/ethyl acetate = 6:4); [α] = −88.2; IR (neat) 3274, 2936, 1745, 1724 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.06 (d, *J* = 3.6 Hz, 1H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.68 (d, *J* = 3.6 Hz, 1H), 4.42 (d, *J* = 3.6 Hz, 1H), 4.27−4.11 (m, 4H), 3.60 (AB quartet, *J* = 16.2 Hz, 2H), 2.50 (t, *J* = 2.4 Hz, 1H), 1.48 (s, 3H), 1.34 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.8, 166.8, 112.5, 105.8, 84.9, 83.2, 81.9, 75.6, 61.1, 58.0, 47.2, 26.8, 26.4, 14.0. Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.69; H, 6.41. Found: C, 57.75; H, 6.32.

General Procedure for the Preparation of Aromatic β-Keto Esters 7a−f. A mixture of aromatic aldehyde (1 mmol) and ethyl diazoacetate (1.5 mmol) was stirred for 10 min under a nitrogen atmosphere at room temperature. Activated alumina (10 times the weight of aldehyde compound, activated at 200 °C at 3 mm of Hg for 4 h prior to use) was added, and the stirring was continued in the solid phase until starting was consumed. The solid mass was then chromatographed on a column with a short plug of silica gel and eluted with ethyl acetate. Evaporation of solvent furnished product that was further purified by chromatography to give aromatic β-keto ester.

Benzenepropanoic acid, 2-*O*-(4′-methoxybenzyl)-β-oxoethyl ester (7a): thick oil; 73% yield; R_f = 0.38 (PE/ethyl acetate = 7:3); IR (neat) 1730, 1676, 1608, 1513 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.46 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.02 (m, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 5.09 (s, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.95 (s, 2H), 3.82 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 193.8,168.4, 159.9, 158.5, 134.7, 131.3, 129.6, 121.0, 114.3, 113.0, 70.6, 61.2, 55.5, 50.7, 14.2. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.51; H, 6.09. Found: C, 69.42; H, 5.95.

Benzenepropanoic acid, 2-*O*-(2′-methoxybenzyl)-*β*-oxoethyl ester (7b): thick oil; 75% yield; $R_f = 0.37$ (PE/ethyl acetate = 7:3); IR (neat) 1725, 1693, 1601, 1489 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, $J = 7.8$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.05−6.90 (m, 5H), 5.21 (s, 2H), 4.08 (q, $J = 7.2$ Hz, 2H), 4.01 (s, 2H), 3.87 (s, 3H), 1.17 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 167.0, 158.0, 156.8, 134.4, 131.0, 129.7, 129.3, 128.8, 120.8, 114.0, 113.9, 70.3, 60.8, 55.2, 50.4, 13.9. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.51; H, 6.09. Found: C, 69.63; H, 6.13.

Benzenepropanoic acid, 2-*O*-(3′,4′-methylenedioxybenzyl)-5-methyl-*β*-oxoethyl ester (7c): thick oil; 76% yield; $R_f = 0.36$ (PE/ethyl acetate = 7:3); IR (neat) 1737, 1671, 1609, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, $J = 2.0$ Hz, 1H), 7.24 (dd, $J = 7.8$, 2.0 Hz, 1H), 6.90−6.75 (m, 4H), 5.98 (s, 2H), 5.02 (s, 2H), 4.10 (q, $J = 6.9$ Hz, 2H), 3.95 (s, 2H), 2.29 (s, 3H), 1.19 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 168.0, 158.1, 148.0, 147.1, 135.0, 131.3, 130.3, 129.7, 121.3, 112.7, 108.3, 108.2, 101.1, 70.6, 60.9, 50.4, 20.2, 14.0. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.61. Found: C, 67.52; H, 5.58.

Benzenepropanoic acid, 2-*O*-(3′-methoxybenzyl)-*β*-oxoethyl ester (7d): thick oil; 71% yield; $R_f = 0.39$ (PE/ethyl acetate = 7:3); IR (neat) 1725, 1693, 1601, 1489 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.47−7.24 (m, 3H), 7.04−6.87 (m, 4H), 5.15 (d, $J = 7.2$ Hz, 2H), 4.09 (m, 2H), 3.95 (s, 2H), 3.82 (s, 3H), 1.18 (t, $J = 6.9$ Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 168.0, 158.2, 156.2, 137.4, 134.4, 129.7, 129.3, 127.9, 120.8, 114.0, 113.9, 112.7, 70.4, 60.8, 55.0, 50.4, 14.0. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.51; H, 6.09. Found: C, 69.46; H, 6.17.

Benzenepropanoic acid, 2-*O*-(benzyl)-*β*-oxoethyl ester (7e). thick oil; 77% yield; $R_f = 0.40$ (PE/ethyl acetate = 7:3); IR (neat) 1738, 1673, 1597, 1483 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.50−7.30 (m, 6H), 7.09−6.92 (m, 2H), 5.17 (s, 2H), 4.10 (q, $J = 7.2$ Hz, 2H), 3.98 (s, 2H), 1.17 (t, $J = 7.2$ Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 168.0, 158.0, 135.7, 134.4, 131.0, 128.7, 128.5, 128.2, 127.4, 120.9, 112.7, 70.5, 60.8, 50.4, 13.9. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 72.56; H, 5.94.

Benzenepropanoic acid, 2-*O*-(methyl)-*β*-oxoethyl ester (7f): thick oil; 74% yield; $R_f = 0.42$ (PE/ethyl acetate = 7:3); IR (neat) 1739, 1671, 1598, 1483 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.51 (dt, $J = 7.5$, 1.8 Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 7.5$ Hz, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 3.97 (s, 2H), 3.89 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 168.0, 159.0, 134.5, 130.9, 120.7, 111.4, 60.8, 55.5, 50.5, 40.0. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.30. Found: C, 64.73; H, 6.24.

General Procedure for the Synthesis of α-Diazo *β*-Keto Esters 3c−f, 13b, and 8a−f. To a stirred solution of *β*-keto ester (1 mmol) in dry acetonitrile (30 mL) were added triethylamine (2 mmol) and methanesulfonyl azide (1.1 mmol). The reaction mixture was stirred at room temperature for 3 h and quenched with aqueous sodium hydroxide (2 M; 1 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried (Na_2SO_4) and evaporated on a rotary evaporator to give thick oil, which on column chromatography (PE/ethyl acetate 19:1) yielded α-diazo *β*-keto ester.

Ethyl 6-deoxy-6-diazo-1,2-*O*-isopropylidene-3-*O*-(3′,4′-methylenedioxybenzyl)-α-D-*xylo*-hept-5-ulofuranuronate (3c): white solid; mp 61−63 °C; 77% yield; $R_f = 0.34$ (PE/ethyl acetate = 6:4); $[\alpha]_D = +12.1$ (*c* 0.25, $CHCl_3$); IR (Nujol) 2138, 1778,1728 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.70 (m, 3H), 6.13 (d, $J = 3.6$ Hz, 1H), 5.96 (s, 2H), 5.42 (d, $J = 3.6$ Hz, 1H), 4.62 (d, $J = 3.6$ Hz, 1H), 4.56 (d, $J = 11.7$ Hz, 1H), 4.43 (d, $J = 3.6$ Hz, 1H), 4.21 (d, $J = 11.7$ Hz, 1H), 4.20−4.10 (m, 2H), 1.50 (s, 3H), 1.35 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.0, 160.6, 147.7, 147.4, 130.7, 122.0, 112.4, 108.6, 107.7, 105.4, 101.0, 83.4, 82.6, 81.2, 71.5, 61.5, 27.0, 26.5, 14.0. Anal. Calcd for $C_{20}H_{22}N_2O_9$: C, 55.29; H, 5.07. Found: C, 55.16; H, 5.15.

Ethyl 6-deoxy-6-diazo-3-*O*-(3′,4′-dimethoxybenzyl)-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-ulofuranuronate (3d): white solid; mp 66−68 °C; 75% yield; $R_f = 0.30$ (PE/ethyl acetate = 6:4); $[\alpha]_D = +16.1$ (*c* 0.25, $CHCl_3$); IR (Nujol) 2143, 1780, 1713 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.81−6.77 (m, 3H), 6.12 (d, $J = 3.6$ Hz, 1H), 5.40 (d, $J = 3.6$ Hz, 1H), 4.63 (d, $J = 12.3$ Hz, 1H), 4.61(d, $J = 3.6$ Hz, 1H), 4.48 (d, $J = 3.6$ Hz, 1H), 4.28 (d, $J = 12.3$ Hz, 1H), 4.21−4.00 (m, 2H), 3.87 (s, 6H), 1.50 (s, 3H), 1.34 (s, 3H), 1.26 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.2, 160.6, 148.9, 148.8, 129.4, 120.9, 112.5, 111.3, 110.5, 105.4, 83.5, 82.6, 81.5, 71.8, 61.5, 55.8, 55.7, 27.1, 26.5, 14.1. Anal. Calcd for $C_{21}H_{26}N_2O_9$: C, 56.01; H, 5.77. Found: C, 56.11; H, 5.85.

Ethyl 3-*O*-(4′-carbmethoxybenzyl)-6-deoxy-6-diazo-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-ulofuranuronate (3e): white solid; mp 103−105 °C; 73% yield; $R_f = 0.32$ (PE/ethyl acetate = 6:4); $[\alpha]_D = +3.2$ (*c* 0.25, $CHCl_3$); IR (Nujol) 2142, 1777, 1713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 6.14 (d, $J = 3.6$ Hz, 1H), 5.45 (d, $J = 4.0$ Hz, 1H), 4.72 (d, $J = 13.0$ Hz, 1H), 4.65 (d, $J = 4.0$ Hz, 1H), 4.48 (d, $J = 3.6$ Hz, 1H), 4.42 (d, $J = 13.0$ Hz, 1H), 4.12 (m, 2H), 3.91 (s, 3H), 1.50 (s, 3H), 1.34 (s, 3H), 1.23 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.0, 166.5, 160.6, 142.0, 129.7, 127.6, 112.5, 105.4, 83.4, 82.5, 82.4, 71.2, 61.6, 52.1, 27.0, 26.5, 14.0. Anal. Calcd for $C_{21}H_{24}N_2O_9$: C, 56.25; H, 5.36. Found: C, 56.16; H, 5.42.

Ethyl 6-deoxy-6-diazo-1,2-*O*-isopropylidene-3-*O*-(4′-nitrobenzyl)-α-D-*xylo*-hept-5-ulofuranuronate (3f): yellowish solid; mp 107−109 °C; 75% yield; $R_f = 0.31$ (PE/ethyl acetate = 6:4); $[\alpha]_D = +9.4$ (*c* 0.25, $CHCl_3$); IR (Nujol) 2140, 1793, 1716 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, $J = 8.7$ Hz, 2H), 7.41 (d, $J = 8.7$ Hz, 2H), 6.16 (d, $J = 3.9$ Hz, 1H), 5.49 (d, $J = 3.3$ Hz, 1H), 4.78 (d, $J = 13.8$ Hz, 1H), 4.66 (d, $J = 3.9$ Hz, 1H), 4.52 (d, $J = 13.8$ Hz, 1H), 4.51 (d, $J = 3.3$ Hz, 1H), 4.30−4.20 (m, 2H), 1.52 (s, 3H), 1.35 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.9, 160.6, 147.4, 144.3, 127.9, 123.4, 112.6, 105.3, 83.2, 83.0, 82.3, 75.7, 70.5, 61.7, 27.0, 26.5, 14.1. Anal. Calcd for $C_{19}H_{21}N_3O_9$: C, 52.41; H, 4.82. Found: C, 52.53; H, 4.91.

Ethyl 6-deoxy-6-diazo-1,2-*O*-isopropylidene-3-*O*-(propargyl)-α-D-*xylo*-hept-5-ulofuranuronate (13b): thick oil; 74% yield; $R_f = 0.33$ (PE/ethyl acetate = 6:4); $[\alpha] = +39.2$; IR (neat) 2930, 2138, 1744, 1714 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.11 (d, $J = 3.6$ Hz, 1H), 5.55 (d, $J = 3.6$ Hz, 1H), 4.71 (d, $J = 3.6$ Hz, 1H), 4.65 (d, $J = 3.6$ Hz, 1H), 4.32 (q, $J = 6.9$ Hz, 2H), 4.22 (dq, $J = 15.9$, 2.4 Hz, 2H), 2.41 (t, $J = 2.4$ Hz, 1H), 1.54 (s, 3H), 1.36 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.8, 161.0, 112.5, 105.3, 83.4, 82.2, 82.02, 78.3, 74.9, 61.6, 57.3, 27.0, 26.5, 14.2. Anal. Calcd for $C_{15}H_{18}N_2O_7$: C, 53.25; H, 5.32. Found: C, 53.18; H, 5.41.

Benzenepropanoic acid, 2-*O*-(4′-methoxybenzyl)-α-diazo-*β*-oxoethyl ester (8a): thick oil; 77% yield; $R_f = 0.33$ (PE/ethyl acetate = 7:3); IR (neat) 2133, 1737, 1682, 1614, 1512 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (dt, $J = 7.8$, 1.5 Hz, 1H), 7.33 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.01 (dt, $J = 7.8$, 1.5 Hz, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 2H), 5.00 (s, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 1.14 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.1, 160.6, 159.2, 156.0, 132.1, 128.6, 128.4, 128.3, 120.6, 113.7, 112.0, 77.0, 70.1, 61.0, 55.0, 13.9. Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.40; H, 5.08. Found: C, 64.32; H, 5.14.

Benzenepropanoic acid, 2-*O*-(2′-methoxybenzyl)-α-diazo-*β*-oxoethyl ester (8b): thick oil; 76% yield; $R_f = 0.32$ (PE:ethyl acetate = 7:3); IR (neat) 2136, 1727, 1693, 1600, 1490 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43−7.26 (m, 4H), 7.03−6.87 (m, 4H), 5.13 (s, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.84 (s, 3H), 1.10 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.2, 160.8, 156.4, 156.2, 132.3, 128.7, 128.5, 127.7, 120.7, 120.5, 112.3, 110.0, 77.2, 65.7, 61.2, 55.2, 14.0. Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.40; H, 5.08. Found: C, 64.33; H, 5.02.

Benzenepropanoic acid, 2-*O*-(3′4′-methylenedioxybenzyl)-α-diazo-*β*-oxoethyl ester (8c): thick oil; 75% yield; $R_f = 0.31$ (PE/ethyl acetate = 7:3); IR (neat) 2134, 1726, 1692,

1599, 1487 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26−7.13 (m, 3H), 6.84−6.76 (m, 3H), 5.96 (s, 2H), 4.93 (s, 2H), 4.21 (q, J = 7.2 Hz, 2H), 2.29 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.1, 159.2, 153.9, 147.8, 147.6, 132.7, 130.4, 130.3, 128.9, 128.1, 120.7, 112.3, 108.1, 107.9, 101.0, 70.5, 61.2, 42.7, 20.2, 14.0. Anal. Calcd for $C_{20}H_{18}N_2O_6$: C, 62.82; H, 4.71. Found: C, 62.91; H, 4.79.

Benzenepropanoic acid, 2-*O*-(3′-methoxybenzyl)-α-diazo-*β*-oxo-ethyl ester (8d): thick oil; 73% yield; R_f = 0.34 (PE/ethyl acetate = 7:3); IR (neat) 2138, 1727, 1693, 1610, 1495 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46−7.28 (m, 4H), 7.07−6.89 (m, 4H), 5.07 (s, 2H), 4.12 (q, J = 7.0 Hz, 2H), 3.84 (s, 3H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 160.6, 158.4, 156.4, 156.2, 134.3, 128.8, 128.7, 127.7, 124.8, 120.7, 120.5, 112.3, 110.5, 65.8, 61.2, 55.3, 42.8, 14.0. Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.40; H, 5.08. Found: C, 64.51; H, 5.12.

Benzenepropanoic acid, 2-*O*-(benzyl)-α-diazo-*β*-oxoethyl ester (8e). thick oil; 76% yield; R_f = 0.35 (PE/ethyl acetate = 7:3); IR (neat) 2139, 1726, 1692,1599, 1487 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.30 (m, 7H), 7.08−6.92 (m, 2H), 5.08 (s, 2H), 4.12 (q, J = 7.2 Hz, 2H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.3, 160.8, 156.1, 136.5, 132.3, 128.6, 128.5, 127.9, 126.9, 120.9, 112.2, 70.5, 61.2, 50.8, 14.0. Anal. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.94. Found: C, 66.53; H, 4.78.

Benzenepropanoic acid, 2-*O*-(methyl)-α-diazo-*β*-oxo-ethyl ester (8f): thick oil; 75% yield; R_f = 0.37 (PE/ethyl acetate = 7:3); IR (neat) 2137, 1728, 1694,1599, 1488 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (dt, J = 7.5, 1.8 Hz, 1H), 7.32 (dd, J = 7.5, 1.8 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.0, 160.8, 156.7, 132.2, 128.4, 120.5, 110.6, 77.0, 61.2, 55.4, 14.0. Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.83. Found: C, 58.19; H, 4.96.

General Procedure for the Decomposition of Sugar α-Diazo *β*-Keto Ester. A solution of α-diazo *β*-keto ester **3c**−**f**, **13b** (0.200 mmol), and $Rh_2(OAc)_4$ (0.002 mmol) in benzene (5 mL) under N_2 atmosphere was refluxed for 10−30 min (for electron-rich substituents the reaction takes 30 min and for electron-deficient substituents it takes 10 min only). On cooling, the reaction mixture was directly loaded onto a silica gel column and with PS-ethyl acetate to afford, first, bicycle **5**; further elution gave the isomeric bicycle **4**. In case of **13b** only **14b** was obtained.

Ethyl 3,6-anhydro-1,2-*O*-isopropylidine-5-*O*-(3′,4′-methylenedioxybenzyl)-α-D-*xylo*-hept-5-enofuranuronate (4c): thick oil; 75% yield; R_f = 0.44 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = +19.6 (*c* 0.25, $CHCl_3$); IR (neat) 1717, 1654 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (d, J = 1.5 Hz, 1H), 6.87 (dd, J = 6.5, 1.5 Hz, 1H), 6.77 (d, J = 6.5 Hz, 1H), 5.96 (s, 2H), 5.94 (d, J = 3.3 Hz, 1H), 5.48 (d, J = 6.5 Hz, 1H), 5.05 (AB quartet, J = 12 Hz, 2H), 4.85−4.81 (m, 2H), 4.30 (q, J = 7.3 Hz, 2H), 1.51 (s, 3H), 1.37 (s, 3H), 1.31 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 147.8, 147.5, 146.1, 131.0, 130.1, 121.1, 113.5, 108.1, 106.0, 101.0, 85.0, 83.8, 82.7, 72.9, 61.1, 27.7, 26.7, 14.2. Anal. Calcd for $C_{20}H_{22}O_9$: C, 59.11; H, 5.41. Found: C, 59.29; H, 5.32.

Ethyl 3,6-anhydro-5-*O*-(3′,4′-dimethoxybenzyl)-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranuronate (4d): thick oil; 76% yield; R_f = 0.42 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = +22.2 (*c* 9.25, $CHCl_3$); IR (neat) 1717, 1652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99−6.93 (m, 2H), 6.84 (d, J = 8.1 Hz, 1H), 5.93 (d, J = 3.6 Hz, 1H), 5.48 (d, J = 6.3 Hz, 1H), 5.10 (AB quartet, J = 12.0 Hz, 2H), 4.83 (m, 2H), 4.28 (q, J = 6.9 Hz, 2H), 3.88 (s, 6H), 1.51 (s, 3H), 1.37 (s, 3H), 1.32 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 149.0, 148.9, 146.3, 131.0, 128.9, 120.0, 113.5, 110.9, 110.8, 106.0, 85.0, 83.7, 82.6, 73.0, 60.9, 55.8, 55.7, 27.6, 26.7, 14.2. Anal. Calcd for $C_{21}H_{26}O_9$: C, 59.71; H, 6.16. Found: C, 59.62; H, 6.22.

Ethyl 3,6-anhydro-5-*O*-(4′-carbmethoxybenzyl)-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranuronate (4e): thick oil; 31% yield; R_f = 0.43 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = +42.7 (*c* 0.25, $CHCl_3$); IR (neat) 1721, 1656 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 5.92 (d, J = 3.0 Hz, 1H), 5.49 (d, J = 6.5 Hz, 1H), 5.22 (AB quartet, J = 12.5 Hz, 2H), 4.87 (d, J = 3.0 Hz, 1H), 4.84 (d, J = 6.5 Hz, 1H), 4.31 (q, J = 6.5 Hz, 2H), 3.95 (s, 3H), 1.51 (s, 3H), 1.36 (s, 3H), 1.29 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 159.7, 145.8, 141.4, 130.1, 129.8, 129.4, 128.0, 127.3, 126.7, 113.1, 105.3, 84.9, 84.3, 83.8, 72.1, 61.1, 52.5, 27.6, 26.6, 14.4. Anal. Calcd for $C_{21}H_{24}O_9$: C, 60.00; H, 5.71. Found: C, 60.12; H, 5.65.

Ethyl 3,6-anhydro-6-(4′-carbmethoxybenzyl)-1,2-*O*-isopropylidene-α-D-*gluco*-hept-5-ulofuranuronate (5e): thick oil; 50% yield; R_f = 0.50 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = +32.4 (*c* 0.25, $CHCl_3$); IR (neat) 1778, 1721 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 5.95 (d, J = 3.5 Hz, 1H), 4.89 (d, J = 3.0 Hz, 1H), 4.25−4.18 (m, 4H), 3.93 (s, 3H), 3.35 (AB quartet, J = 14.0 Hz, 2H), 1.48 (s, 3H), 1.36 (s, 3H), 1.27 (t, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.6, 166.7, 139.2, 130.8, 130.5, 130.0, 129.6, 129.1, 113.5, 107.7, 86.5, 85.3, 82.7, 62.6, 52.0, 40.4, 27.3, 26.5, 13.9. Anal. Calcd for $C_{21}H_{24}O_9$: C, 60.00; H, 5.71. Found: C, 60.22; H, 5.79.

Ethyl 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-(4′-nitrobenzyl)-α-D-*xylo*-hept-5-enofuranuronate (4f): thick oil; 26% yield; R_f = 0.42 (PE/ethyl acetate = 6:4); $[\alpha]_D$ = +32.1 (*c* 0.25, $CHCl_3$); IR (neat) 1717, 1654 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 5.92 (d, J = 3.5 Hz, 1H), 5.26 (d, J = 6.4 Hz, 1H), 5.20 (AB quartet, J = 16.6 Hz, 2H), 4.91 (d, J = 6.4 Hz, 1H), 4.86 (d, J = 3.5 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.51 (s, 3H), 1.37 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 145.5, 143.6, 127.4, 123.7, 113.7, 84.9, 84.0, 82.7, 71.6, 61.3C, 27.7, 26.7, 14.2. Anal. Calcd for $C_{19}H_{21}NO_9$: C, 56.01; H, 5.15. Found: C, 56.18; H, 5.24.

Ethyl 3,6-anhydro-1,2-*O*-isopropylidene-6-(4′-nitrobenzyl)-α-D-*gluco*-hept-5-ulofuranuronate (5f): thick oil; 56% yield; R_f = 0.49 (PE:ethyl acetate = 6:4); $[\alpha]_D$ = +30.4 (*c* 0.25, $CHCl_3$); IR (neat) 1778, 1744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 5.96 (d, J = 3.3 Hz, 1H), 4.90 (d, J = 3.3 Hz, 1H), 4.38 (d, J = 4.0 Hz, 1H), 4.32 (d, J = 4.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.31 (s, 2H), 1.43 (s, 3H), 1.33 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 166.5, 147.3, 141.6, 131.7, 131.3, 123.4, 123.0, 113.6, 107.9, 86.0, 85.4, 83.0, 78.6, 62.8, 40.0, 27.3, 26.6, 13.9. Anal. Calcd for $C_{19}H_{21}NO_9$: C, 56.01; H, 5.15. Found: C, 56.12; H, 5.06.

Ethyl 3,6-anhydro-1,2-*O*-isopropylidene-6-(allenyl)-α-D-*gluco*-hept-5-ulofuranuronate (14b): thick oil; 77% yield; R_f = 0.44 (PE/ethyl acetate = 6:4); $[\alpha]$ = +90.4; IR (neat) 1780, 1746, 1631 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (d, J = 3.4 Hz, 1H), 5.52 (t, J = 6.5 Hz, 1H), 5.08 (d, J = 6.5 Hz, 2H), 4.96 (d, J = 3.4 Hz, 1H), 4.85 (d, J = 3.3 Hz, 1H), 4.61 (d, J = 3.3 Hz, 1H), 4.26 (q, J = 7.4 Hz, 2H), 1.51 (s, 3H), 1.40 (s, 3H), 1.30 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7, 199.3, 166.3, 113.5, 107.8, 89.0, 85.2, 83.4, 82.9, 80.1, 78.8, 62.5, 27.3, 26.6, 13.9. Anal. Calcd for $C_{15}H_{18}O_7$: C, 58.06; H, 5.80. Found: C, 58.15; H, 5.72.

General Procedure for the Decomposition of Aromatic α-Diazo *β*-Keto Ester. A solution of α-diazo *β*-keto ester **8a**−**f** (0.200 mmol) and $Rh_2(OAc)_4$ (0.002 mmol) in benzene (5 mL) under N_2 atmosphere was refluxed for 10−30 min (for electron-rich substituents the reaction takes 30 min and for electron-deficient substituents it takes 10 min only). On cooling, the reaction mixture was directly loaded onto a silica gel column and with PE/ethyl acetate to afford, first, bicycle **9**; further elution gave the isomeric bicycle **10**.

2-Benzofurancarboxylic acid, 3-*O*-(4′-methoxybenzyl)-ethyl ester (9a): thick oil; 76% yield; R_f = 0.43 (PE/ethyl acetate = 7:3); IR (neat) 1710, 1613, 1514 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.6, 1.3 Hz, 1H), 7.47 (dt, J = 7.6, 1.3 Hz, 1H), 7.41−7.20 (m, 4H), 6.87 (d, J = 7.5 Hz, 2H), 5.38 (s, 2H), 4.45 (q, J = 6.9 Hz, 2H), 3.97 (s, 3H), 1.43 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 159.4, 153.1, 148.3, 132.4, 129.9, 128.3, 124.3, 123.2, 121.0, 113.9, 112.8, 76.2, 61.2, 55.4, 14.7. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.52. Found: C, 69.82; H, 5.41.

2-Benzofurancarboxylic acid, 3-*O*-(2′-methoxybenzyl)-ethyl ester (9b): thick oil; 73% yield; R_f = 0.42 (PE/ethyl acetate = 7:3); IR (neat) 1714, 1617, 1514 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (bd, J = 8.1 Hz, 1H), 7.58−7.38 (m, 3H), 7.34−7.19 (m, 2H), 6.96 (dt, J = 7.5, 1.0 Hz, 1H), 6.86 (bd, J = 8.1 Hz, 1H), 5.49 (s, 2H), 4.44 (q, J = 7.2 Hz, 2H), 3.77 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 157.0, 153.1, 148.5, 132.1, 129.4, 129.3, 128.1, 122.9, 121.1, 120.3, 112.5, 110.1, 71.3, 60.9, 55.1, 14.2. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.52. Found: C, 69.79; H, 5.39.

2-Benzofurancarboxylic acid, 3-*O*-(3′,4′-methylenedioxybenzyl)-5-methylethyl ester (9c): thick oil; 76% yield; R_f = 0.41 (PE/ethyl acetate = 7:3); IR (neat) 1719, 1618, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (bs, 1H), 7.37 (bd, J = 8.5 Hz, 1H), 7.23 (bd, J = 8.5 Hz, 1H), 7.01 (bs, 1H), 6.92 (bd, J = 8.4 Hz, 1H), 6.78 (bd, J = 8.4 Hz, 1H), 5.97 (s, 2H,), 5.33 (s, 2H), 4.46 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 151.7, 147.8,-147.7, 132.8, 132.4 130.8, 130.4, 129.9, 122.8, 121.9, 120.2, 112.3, 108.8, 108.1, 101.1, 76.0, 61.0, 21.2, 14.4. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.08. Found: C, 67.63; H, 5.18.

2-Benzofurancarboxylic acid, 3-*O*-(3′-methoxybenzyl)-ethyl ester (9d): thick oil; 45% yield; R_f = 0.44 (PE/ethyl acetate = 7:3); IR (neat) 1718, 1618, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (bt, J = 7.8 Hz, 1H), 7.48−7.40 (m, 3H), 7.26, (m, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.87 (dd, J = 7.8, 1.8 Hz, 2H), 5.41 (s, 2H), 4.46 (q, J = 7.2 Hz, 2H), 3.80 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 159.4, 153.1, 148.3, 138.1, 129.8, 129.5, 128.7, 128.2, 123.1, 120.9, 113.8, 113.3, 112.7, 75.9, 61.1, 55.2, 14.4. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.52. Found: C, 69.81; H, 5.68.

2-Benzofurancarboxylic acid, 3-oxo-2-(3′-methoxybenzyl)ethyl ester (10d): thick oil; 33% yield; R_f = 0.40 (PE/ethyl acetate = 7:3); IR (neat) 1748, 1725, 1610, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.55 (m, 2H), 7.26−7.01 (m, 4H), 6.86−6.70 (m, 1H), 6.73−6.67 (m, 1H), 4.22 (q, J = 6.9 Hz, 2H), 3.73 (s, 3H), 3.48 (AB quartet, J = 14.7 Hz, 2H), 1.23 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 172.1, 165.4, 159.2, 138.4, 131.3, 129.1, 124.7, 122.6, 115.7, 113.5, 113.3, 112.9, 91.3, 62.6, 55.1, 39.8, 14.0. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.52. Found: C, 69.78; H, 5.48.

2-Benzofurancarboxylic acid, 3-*O*-benzylethyl ester (9e): thick oil; 46% yield; R_f = 0.45 (PE/ethyl acetate = 7:3); IR (neat) 1715, 1612, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.4, 1.5 Hz, 1H), 7.54−7.21 (m, 8H), 5.46 (s, 2H), 4.44 (q, J = 6.9 Hz, 2H), 1.42 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 153.1, 148.2, 136.5, 132.2, 128.4, 128.3, 127.9, 123.1, 122.7, 120.9, 112.7, 76.1, 61.0, 14.3. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40. Found: C, 72.81; H, 5.28.

2-Benzofurancarboxylic acid, 3-oxo-2-benzylethyl ester (10e): thick oil; 30% yield; R_f = 0.41 (PE/ethyl acetate = 7:3); IR (neat) 1745, 1614, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.45 (m, 2H), 7.32−7.02 (m, 7H), 4.20 (q, J = 6.9 Hz, 2H), 3.51 (AB quartet, J = 14.1 Hz, 2H), 1.21 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 172.1, 165.4, 138.4, 133.3, 130.3, 128.1, 127.9, 127.2, 124.7, 122.5, 119.6, 113.3, 91.4, 62.6, 39.8, 13.9. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40. Found: C, 73.14; H, 5.58.

2-Benzofurancarboxylic acid, 3-*O*-methylethyl ester (9f): tThick oil; 65% yield; R_f = 0.46 (PE/ethyl acetate = 7:3); IR (neat) 1719, 1618, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.8, 1.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.24 (dt, J = 7.8, 1.2 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 4.24 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 153.0, 149.4, 128.2, 123.0, 121.0, 112.7, 61.4, 60.9, 14.3. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 64.63; H, 5.56.

Acknowledgment. We are grateful to Prof. N. S. Narasimhan and Prof. M. S. Wadia for the helpful discussions. N.P.K. is thankful to UGC for the JRF. The financial support from UGC, New Delhi, to procure a high field (300 MHz) NMR facility under the CAS program is also gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **3c−f**, **4c−f, 5c−f, 8a−f, 9a−f, 10a−f, 13b, 14b**. This material is available free of charge via the Internet at http:// pubs.acs.org.

JO010431F