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Claudio L. Donnici [a], Elaine Henriques Teixeira Pereira [a], Júlio C. Dias Lopes [a], Liliana Marzorati [b] & Blanka Wladislaw [b]

[a] Chemistry Department, Institute of Exact Sciences, Federal University of Minas Gerais, Belo Horizonte, Brazil

[b] Institute of Chemistry, University of São Paulo, São Paulo, Brazil

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SELECTIVE SULFENYLATIVE DESULFONYLATION OR DECARBALKOXYLATION OF α-SULFONYL MALONATES WITH DABCO OR Bu_3N: REACTIVITY AND CONFORMATIONAL ANALYSIS

Claudio L. Donnici,[1] Elaine Henriques Teixeira Pereira,[1] Júlio C. Dias Lopes,[1] Liliana Marzorati,[2] and Blanka Wladislaw[2]

[1]*Chemistry Department, Institute of Exact Sciences, Federal University of Minas Gerais, Belo Horizonte, Brazil*

[2]*Institute of Chemistry, University of São Paulo, São Paulo, Brazil*

The study on reactivity of several α-substituted α-sulfonyl malonates toward 1,4-diazabicyclo[2.2.2]octane (DABCO) and Bu_3N is described. The reactivity with DABCO revealed the possible competition between decarbalkoxylation and unexpected desulfonylation, depending on the α-substituent, because of sterical hindrance around the electrophilic centers (SO_2 and CO_2R). The derivatives with crowded α-substituents suffer selective desulfonylation, and a novel and efficient desulfonylation method can be proposed. The dependence of the reactivity of α-sulfonyl malonates on the sterical hindrance around the electrophilic centers is confirmed by conformational analysis (Macromodel/MM2* and Mopac/MP3). The carbanionic mechanism is proved because the corresponding protonated, deuterated, and sulfenylated products were obtained by addition of the corresponding electrophilic agents. Bu_3N showed itself to be a novel selective decarbalkoxylation agent for any α-substituted α-sulfonyl malonate.

Keywords: Conformational analysis; DABCO; decarbalkoxylation–desulfonylation; regioselectivity; α-sulfonyl-malonates; tributylamine

INTRODUCTION

Activated compounds such as malonate esters, α-keto-esters, α-cyano esters, and α-aryl(alkyl)sulfonyl esters find considerable utility in organic synthesis.[1,2] Traditionally, the malonic ester synthesis is one of the most important examples of the synthesis of higher homologous esters, starting from malonic ester.[3] Nevertheless, these conditions sometimes are not selective, and substrates containing either acid- or base-sensitive groups cannot be employed in this hydrolysis–decarboxylation process. Krapcho[3,4] developed an easier methodology for the dealkoxycarbonylation of

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Address correspondence to Claudio L. Donnici, Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627, BH, MG, Brazil, 31270-901. E-mail: cdonnici@terra.com.br

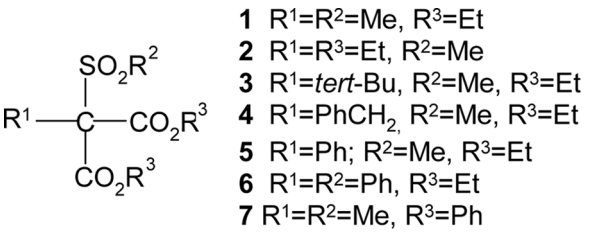
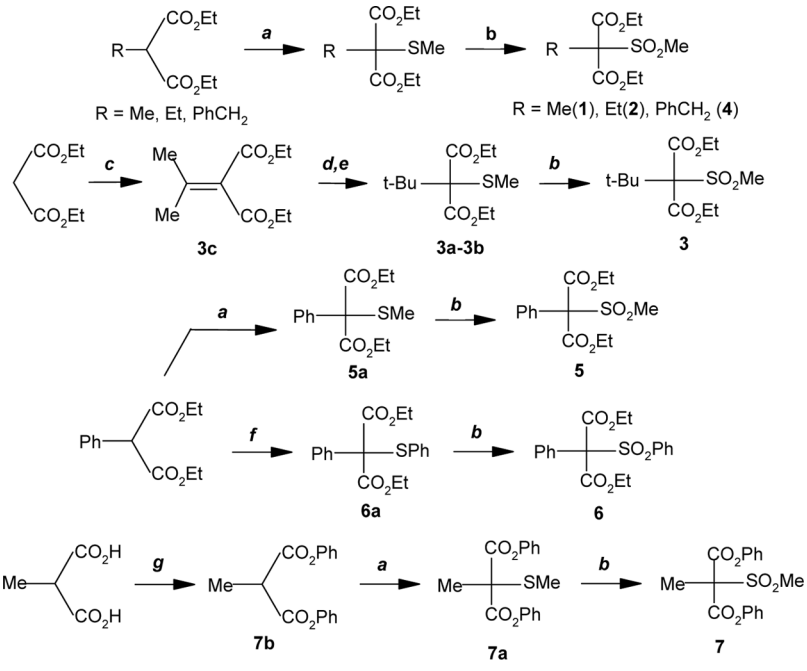


Figure 1. Synthesized sulfonyl malonates.

malonate esters and other activated compounds: the use of anhydrous salts in dipolar aprotic media such as dimethylsulfoxide (DMSO). α-Sulfenylated carboxylic acids exhibit some noteworthy synthetic applications. These compounds are useful for convenient two-step conversion of carboxylic acids to the corresponding ketones;[5] α-sulfonyl carboxylic acids can also be used to generate the corresponding α-keto esters and thioesters.[6,7] Interestingly, Corey, and Lowry reported an anionic decarboxylation of α-sulfonyl carboxylic acids with retention of configuration.[8] Triton-B showed itself to be a very efficient and mild agent for decarbalkoxylation of α-sulfonylmalonates.[9] Miles and Chuang[10] reported that geminal esters treated with 1,4-diazabicyclo[2.2.2]octane (DABCO) in refluxing xylene give decarbalkoxylation products. However, preliminary studies showed that when diethyl α-sulfonylmalonates were treated with DABCO in refluxing toluene, there was competition between decarboxylation and sulfenylation.[11] Despite that, just recently it became possible to continue these investigations and to study this unusual reactivity, as described herein. In fact, the removal of the sulfonyl group from carboxylic derivatives is not so easy, even with the common desulfurative process using Raney nickel,[12] as described by Shioiri and coworkers in the study of the reactivity of some α-benzylsulfonyl acetates.[13] We report herein the results of our study on this dual behavior of some derivatives of α-sulfonyl malonates (Fig. 1) toward DABCO and tributylamine and the conformational analysis of these sulfonyl malonic derivatives. The strong influence of the steric hindrance around the electrophilic center on the reactivity is shown. Even though the desulfonylation could be effected using several different methods (for example, thermal rearrangement,[14] catalyzed reaction with Ru(II),[15,16] via radical-initiated cleavage,[17] by cathodic reduction,[18,19] by oxygenation of an α-sulfonyl carbanion by molybdenum peroxide,[20] by coupling with Grignard reagents in the presence of copper,[21] or by coupling with methyl/phenyl lithium,[22] by treatment with $TiCl_4$[23] or $TiCl_4$-Sm[24]) in our oppinion, the novel desulfonylation method with DABCO developed by us may be a good preparative method for selective desulfonylation in crowded polyfunctionalized molecules.

RESULTS AND DISCUSSION

In the present work, several α-sulfonyl malonates (**1–7**) were synthesized (Scheme 1) starting from the corresponding alkyl or phenyl malonates, which were submitted as a suitable method for sulfenylation (generally NaH/DMSO and $MeSO_2SMe$ or $PhSO_2SPh$) and oxidation (H_2O_2/HOAc), generating the



Scheme 1. Reagents and conditions: (a) NaH/DMSO; rt, $MeSO_2SMe$, 77–85%; (b) H_2O_2/HOAc, reflux, 1.5 h, 62–88%; (c) acetone, $ZnCl_2$, Ac_2O, reflux, 24 h, 58%; (d) MeMgI/ethyl ether, CuCl, 30 min. rt, H_2SO_4/H_2O, 60%; (e) LDA, THF, −78°C, $MeSO_2SMe$, rt, 2 h, 89%; (f) NaH/DMSO, rt; $PhSO_2SPh$, 86%; and (g) phenol, $POCl_3$, 100°C, 30 min, 50%.

corresponding sulfonyl malonates. In fact, the synthesis of the *tert*-butyl analog **3** started from preparation of the diethyl isopropylidenemalonate (40%), followed by the reaction with methyl magnesium bromide in anhydrous diethyl ether (65%) and sulfenylation with lithium diisopropylamide (LDA), (89%). For the synthesis of the diphenyl ester **7**, the diethyl methylmalonate was first submitted to the transesterification reaction with phenol in $POCl_3$ (40%).

The data related to the studies on the reactivity of several α-sulfonyl malonates to to DABCO and tributylamine (Bu_3N) are given in Table 1. With Bu_3N, all α-sulfonyl-malonates gave the decarbalkoxylation products, but under quite vigorous conditions (110°C, 48 h). Therefore, the Krapcho[4] and Triton-B[7] methodologies are milder. The reactivity of α-sulfonyl-malonates to DABCO revealed the possible competition between decarbalkoxylation and desulfonylation: the methyl **1** and ethyl **2** derivatives gave only the decarbethoxylated products **1.1** and **2.1** (69–81%), but the α-benzyl derivative **4** led to partial decarbalkoxylation and desulfonylation (**4.1** and **4.2**: 49–51%). On the other hand, for the α-*tert*-butyl **3** and α-phenyl **5** analogs, only the desulfonylation occurs (**3.4**–**5.4**: 68–83%). The influence of the sterical hindrance exerted by the α-substituents on the reactivity of the α-sulfonylmalonates toward DABCO is strongly noticed, and it can be proposed that the crowd around the electrophilic centers is an important factor, as suggested by Chou and Chang[22] for nucleophilic attack on the sulfonyl sulfur atom. This hypothesis

Table 1. α-Sulfonyl malonates **1–7**, synthesized as described in Scheme 1, and malonates, studied with DABCO and tributylamine

Entry	α-Sulfonyl malonate	Product with DABCO	Yield (%)	Product with tris-butylamine	Yield (%)
		$MeCH(CO_2Et)SO_2Me$[a]			
		1.1	78		
	$MeC(CO_2Et)_2SO_2Me$	$MeCSMe(CO_2Et)SO_2Me$[b]		$MeCH(CO_2Et)SO_2Me$	
1	**1**	**1.2**	72	**1.1**	81
		$MeCSPh(CO_2Et)SO_2Me$[c]			
		1.3	68		
		$EtCH(CO_2Et)SO_2Me$[a]			
		2.1	68		
	$EtC(CO_2Et)_2SO_2Me$	$EtCSMe(CO_2Et)SO_2Me$[b]		$EtCH(CO_2Et)SO_2Me$	
2	**2**	**2.2**	72	**2.1**	69
		$EtCSPh(CO_2Et)SO_2Me$[c]			
		2.3	61		
		t-$BuCH(CO_2Et)_2$[a]			
	t-$BuC(CO_2Et)_2SO_2Me$	**3.4**	68	t-$BuCH(CO_2Et)SO_2Me$	
3	**3**	t-$BuCSMe(CO_2Et)_2$[b]		**3.1**	67
		3.2	42		
		$PhCH_2CH(CO_2Et)_2$[a]	49		
	$PhCH_2C(CO_2Et)_2SO_2Me$	**4.1**		$PhCH_2CH(CO_2Et)SO_2Me$	
4	**4**	$PhCH_2CH(CO_2Et)SO_2Me$[a]	51	**4.1**	70
		4.2			
		$PhCH(CO_2Et)_2$[a]	83		
	$PhC(CO_2Et)_2SO_2Me$	**5.4**		$PhCH(CO_2Et)SO_2Me$	
5	**5**	$PhCSMe(CO_2Et)_2$[b]	62	**5.1**	68
		5.2			
		$PhCH(CO_2Et)SO_2Ph$[a]	72	$PhCH(CO_2Et)SO_2Ph$	
	$PhC(CO_2Et)_2SO_2Ph$	**6.1**		**6.1**	65
6	**6**	$PhCSMe(CO_2Et)SO_2Ph$[b]	68		
		6.2			
		$MeCH(CO_2Ph)SO_2Me$[b]	62	$MeCH(CO_2Ph)SO_2Me$	
	$MeC(CO_2Ph)_2SO_2Me$	**7.1**		**7.1**	60
7	**7**	$MeCH(CO_2Ph)SO_2Me$[c]	60		
		7.2			

[a,b,c]After reaction with DABCO and addition of water,[a] $MeSO_2SMe$,[b] or $PhSO_2SPh$.[c]

[d]All products were characterized by IR, NMR, and mass spectroscopy; isolated yields of products after column chromatography.

can be corroborated by the fact that the diethylmalonate **6**, with steric crowd around the sulfone group, suffered decarbalkoxylation, generating the corresponding decarbalkoxylated products **6.1** (72% yield). The anionic mechanistic pathway can be confirmed by addition of water, or deuterated water, after the decarbalkoxylation/desulfonylation step. Moreover, when electrophilic sulfenylating agents, such as $MeSO_2SMe$ or $PhSO_2SPh$, were added to the reaction mixture, the sulfenylated products were obtained in quite reasonable yields (62–72%).

Finally, a better comprehension of steric hindrance influence on the reactivity could be achieved by a theoretical approach, for example, through the data obtained from the mechanical molecular calculations (Macro Model/MM2*), which showed

different conformational equilibria for the different α-sulfonyl-malonates. The analysis of the preferential conformations for the derivatives **1** (α-methyl), **2** (α-ethyl), **6** (α-phenyl-phenyl sulfonyl), and **7** (α-methyl diphenylester) revealed that those conformers do not have any steric hindrance around the carboxyl groups, and the decarbalkoxylation is favored. For the derivatives **3** (α-*tert*-butyl) and **5** (α-phenyl), the most stable conformations show that the bulky α-*tert*-butyl or α-phenyl groups are closer to the carbalkoxy groups. Additionally, the methylsulfonyl group is very close to one of these carbalkoxy groups, which creates steric hindrance around it, leading preferably to the desulfonylation. For the benzyl derivative **4**, there are two major conformers **4a** and **4b**: the most stable conformer **4a** shows that only one of the carbalkoxy groups is accessible and the decarbalkoxylation is favored, but the conformer **4b** shows steric hindrance around both carbomethoxy groups favors the desulfonylation. In fact, for **4**, both partial decarbalkoxylation and desulfonylation occur. It is remarkable that the analysis of dihedral angles (S−C−C−O: α or β angles) of the studied sulfonyl-malonates generally demonstrate the presence of *gauche* configuration (ca. 60–90°), which can lead to a hiperconjugative interaction π_{co}/σ^*_{c-s}, which makes the C−O bond longer, more polar, and maybe more reactive toward nucleophilic attack. The results obtained from a semi-empirical method (Mopac/PM3) allowed us to calculate the partial atomic charges from the functional groups CO_2R and SO_2R. These data could generate the building of electrostatic potential surfaces, which revealed the existence of a charge-transfer interaction between the molecular orbitals of the sulfonyl and carbonyl groups, $O_{SO_2} \rightarrow \pi_{co}$. Besides the analysis of some dihedral angles from selected malonates, **1** and **3** present angles around 60° between sulfonyl oxygen. The carbonyl carbon also suggests the occurrence of an $O_{SO_2} \rightarrow \pi_{co}$ interaction, as already described.[25] Moreover these semi-empirical data about the sum of the partial atomic charges of the functional groups CO_2R and SO_2R showed that the sulfonyl group must present the higher positive-density charge. Consequently, the sulfonyl group should be the preferred electrophilic center for the DABCO's nucleophilic attack, even though the preferential attack of DABCO is over the carbalkoxyl groups. This contradiction might be explained by the fact that carbonyl carbon has sp_2 geometry, which is more sterically acessible, whereas the sulfur atom of the sulfone group has sp_3 geometry, less sterically acessible to DABCO's attack. Hence, the desulfonylation only occurs when there is a great steric hindrance around the carbalkoxy groups and the α-sulfone group is available, such as for **3** and **5**. A global analysis of the results suggests that in the mechanism of decarbalkoxylation by DABCO, the nucleophilic attack should be on the carbonyl carbon atom, because the dicarbophenoxy derivative **6** suffers decarbalkoxylation, even with the phenyl group being attached to the carboxylic group. It is difficult to propose a nucleophilic mechanism for DABCO on a high eletronic density Csp_2 from an aromatic ring. For the mechanism of desulfonylation, it can be proposed that the nucleophilic attack by DABCO occurs on the alkyl group attached to the sulfone and not on the sulfonyl sulfur atom. All these results reveal that in the reactivity of α-sulfonyl-malonates with DABCO, leading to decarbalkoxylation or desulfonylation, the steric factor is most important for the regioselectivity of DABCO's nucleophilic attack. If there is a very bulky group, only the desulfonylation occurs. Finally, it is noteworthy to point out that because it is rather easy to functionalize any molecule with a

sulfonyl-malonate group, if this group was a crowded one, this novel desulfonylation method with DABCO might be a good preparative method for selective removal of sulfonyl group and possible subsequent functionalization by electrophiles in crowded polyfunctionalized molecules.

EXPERIMENTAL

General

Melting points were determined on a Mettler apparatus and were uncorrected. Starting materials were of the highest commercial quality and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (AC-200 MHz) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Fourier transform–infrared FT-IR spectra were recorded on a Mattson instrument, model Galaxy 3000. Microanalyses were carried out on a Perkin-Elmer CHNS 2400 elemental analyzer.

Compounds **1–7** were prepared from the corresponding malonic diacid or ester derivatives as starting materials according to the synthetic methodology described in Scheme 1. These sulfonylmalonates were obtained, after purification and isolation, in good global yields, and the analysis of the spectroscopic data of the pure compounds are given.

General Procedure for the Reaction of α-Sulfonylmalonates 1–7 with DABCO

A mixture of sulfonylmalonate (10 mmol) and DABCO (50 mmol) in dry toluene (15 mL) was stirred under reflux for 8 h and cooled to room temperature. Water (2 mL) was added, and the mixture was filtered and concentrated under reduced pressure. Silica-gel chromatography (hexane–ethylacetate 8:2 vol/vol) gave the purified products. The reactions underwent subsequent sulfenylation after reaction with DABCO, $MeSO_2SMe$, or $PhSO_2SPh$ (10.5 mmol). The mixture was stirred for 6 h at rt; and the following workup is described.

General Procedure for the Reaction of α-Sulfonylmalonates 1–7 with Tributylamine

A mixture of sulfonyl-malonate (1.0 mmol), tributylamine (18 mmol, 4.0 mL), and *p*-xylene (3 mL) was refluxed for 48 h, cooled to rt, poured into water (10 mL), extracted with CH_2Cl_2 (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a crude product, which was purified by silica-gel column chromatography to afford the decarbalkoxylated product.

Selected Data

Diethyl methyl(methylsulfonyl)malonate (1). Yellowish oil; IR ν_{max} (KBr)/cm^{-1} 1740, 1322, 1152. ^{1}H NMR ($CDCl_3$) δ 4.34 (4H, q, *J* 7.2, OCH_2), 3.29 (3H, s, CH_3SO_2), 1.90 (3H, s, CH_3C), 1.35 (6H, t, *J* 7, $CH_{3diester}$), 1.16 (3H,

t, *J* 7.2, CH_3 alkyl); ^{13}C NMR ($CDCl_3$) δ 164.49, 75.52, 62.86, 39.56, 14.10, 13.75. Anal. calcd. for $C_9H_{16}O_6S$: C, 42.85; H, 6.40. Found: C, 42.79; H, 6.43.

Diethyl ethyl(methylsulfonyl)malonate (2). Yellowish oil; IR ν_{max} (KBr)/cm^{-1} 1739, 1323, 1153. ^1H NMR ($CDCl_3$) δ 4.38 (4H, q, *J* 7.2, OCH_2), 3.24 (3H, s, $MeSO_2$), 2.42 (2H, q, *J* 7.2, CCH_2), 1.33 (6H, t, *J* 7.2, CH_3 diester), 1.16 (3H, t, *J* 7.2, CH_3 alkyl); ^{13}C NMR ($CDCl_3$) δ 164.26, 79.64, 62.60, 40.33, 22.75, 13.45, 9.20. Anal. calcd. for $C_{10}H_{18}O_6S$: C, 45.10; H, 6.82. Found: C, 45.13; H, 6.85.

Diethyl 1,1-dimethylethyl-(methylsulfonyl)malonate (3). Yellowish oil; IR ν_{max} (KBr)/cm^{-1} 1750, 1370, 1310, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.20 (4H, q, *J* 7.0, OCH_2), 3.49 (3H, s, $MeSO_2$), 1.43 (6H, t, *J* 7.0, CH_3 diester), 1.12 (9H, t, *tert*-Bu); ^{13}C NMR ($CDCl_3$) δ 168.43, 107.45, 63.50, 60.80, 43.43, 14.10, 13.83. Anal. calcd. for $C_{12}H_{22}O_6S$: C, 48.96; H, 7.54. Found: C, 49.01; H, 7.58.

Diethyl benzyl(methylsulfonyl)malonate (4). Pale yellow crystals, mp 55–56°C; IR ν_{max} (KBr)/cm^{-1} 1727, 1310, 1146. ^1H NMR ($CDCl_3$) δ 7.4–7.2 (5H, m, H_{Ar}), 4.3–4.0 (4H, m, OCH_2), 3.74 (2H, s, CH_3SO_2), 3.19 (3H, s, CH_2Ph), 1.16 (3H, t, *J* 7.2, CH_3 alkyl); ^{13}C NMR ($CDCl_3$) δ 164.02, 133.64, 130.63, 127.94, 127.33, 81.00, 62.78, 40.27, 33.49, 13.36. Anal. calcd. for $C_{15}H_{20}O_6S$: C, 54.86; H, 6.14. Found: C, 54.89; H, 6.18.

Diethyl phenyl(methylsulfonyl)malonate (5). Colorless crystals, mp 87–88°C; IR ν_{max} (KBr)/cm^{-1} 1760, 1310, 1130. ^1H NMR ($CDCl_3$) δ 7.6–7.5 (2H, m, $H_{Ar-ortho}$), 7.5–7.4 (3H, m, $H_{Ar-para}$), 4.43 (4H, q, *J* 7.0, OCH_2), 3.03 (3H, s, CH_3SO_2), 1.35 (6H, t, *J* 7.0, CH_3 alkyl); ^{13}C NMR ($CDCl_3$) δ 164.15, 129.97, 128.86, 128.80, 128.58, 85.05, 63.52, 40.71, 13.84. Anal. calcd. for $C_{14}H_{18}O_6S$: C, 53.49; H, 5.78. Found: C, 53.54; H, 5.75.

Diethyl phenyl(phenylsulfonyl)malonate (6). Colorless crystals, mp 57–59°C; IR ν_{max} (KBr)/cm^{-1} 1750, 1325, 1140;^1H NMR ($CDCl_3$) δ 7.6–7.2 (10H, m, H_{Ar}), 4.37 (4H, q, *J* 7.2, OCH_2), 1.30 (6H, t, *J* 7.2, CH_3 alkyl); ^{13}C NMR ($CDCl_3$) δ 163.74, 136.68, 133.66, 131.20, 130.16, 129.47, 129.23, 127.99, 127.62, 86.07, 63.08, 13.69. Anal. calcd. for $C_{19}H_{20}O_6S$: C, 60.62; H, 3.59. Found: C, 60.67; H, 3.61.

Diphenyl methyl(methylsulfonyl)malonate (7). Colorless crystals, mp 100–101°C; IR ν_{max} (KBr)/cm^{-1} 1750, 1320, 1140. ^1H NMR ($CDCl_3$) δ 7.5–6.7 (10H, m, H_{Ar}), 3.43 (3H, s, CH_3SO_2), 2.20 (3H, s, CH_3 alkyl); ^{13}C NMR ($CDCl_3$) δ 163.70, 149.90, 129.83, 127.01, 120.86, 76.76, 40.05, 14.88. Anal. calcd. $C_{17}H_{16}O_6S$: C, 58.61; H, 4.63. Found: C, 58.66; H, 4.67.

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