The Reaction of Chlorosulfonyl Isocyanate with Epoxides. A Novel Conversion of Epoxides to Cyclic Carbonates

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The facile reaction of chlorosulfonyl isocyanate (CSI) with epoxides is described. The initially formed 2-chlorosulfonylimino-1,3-dioxolane **2a-e** and *N*-chlorosulfonyl-1,3-oxazolidin-2-one **3a-e** derivatives undergo smooth hydrolysis to yield the corresponding 1,3-dioxolan-2-one **4a-e** and 1,3-oxazolidin-2-one **5a-e** derivatives respectively. This reaction sequence provides a convenient one-pot method for the conversion of epoxides to cyclic carbonates. Substrates such as **1g-i** are exceptions to this otherwise general reaction pathway.

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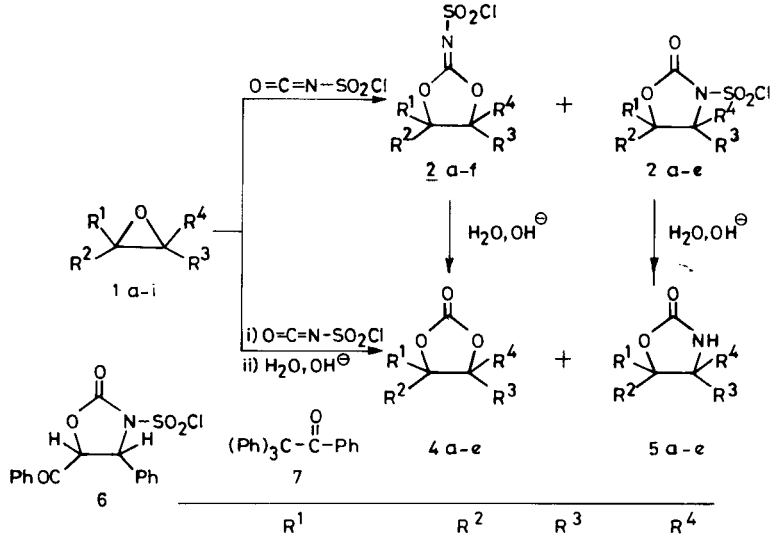
CSI is a highly reactive heterocumulene and a versatile reagent. It has a remarkable utility in the synthesis of a variety of heterocyclic systems and in bringing about many synthetic transformations [1,2]. But so far no attention seems to have been given to study its behaviour towards three membered heterocyclic systems. We have investigated the reaction of CSI with some three membered heterocyclic systems and the results obtained in the reaction of CSI with epoxides are presented in this paper.

Epoxides are known to react with alkyl, aryl, acetyl and sulfonyl isocyanates to give *N*-substituted 1,3-oxazolidin-2-one derivatives [3-7]. These reactions generally occur at elevated temperatures and in the presence of soluble lithium salt-phosphine oxide catalyst. The reaction lacks selectivity as unsymmetrical epoxides are reported to give 4- and 5-isomeric mixtures of oxazolidin-2-ones [4]. In contrast to these observations we have found that CSI reacts readily with epoxides in a facile manner. The reaction is found to be highly selective and proceeds under very mild experimental conditions, without involving the use of a catalyst.

Scheme 1



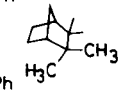
	R^1	R^2	R^3	R^4
1-5 a	Ph	H	Ph	H
1-5 b	H	Ph	Ph	H
1-5 c	H	—— $(CH_2)_6$ ——		H
1-5 d	H	H	H	Ph
1-5 e	COPh	H	Ph	H
1-2 f			H	H
1 g	COPh	H	COPh	H
1 h	COPh	H	P-$NO_2C_6H_4$	H
1 i	Ph	Ph	Ph	Ph

Table 1

Physical Data of 2-Chlorosulfonylimino-1,3-dioxolanes, **2a, 2c, 2e, 2f**

Compound No.	Mp °C	Yield %	Recrystallization Solvents	Formula	Analyses % Calcd. C	H	N	Found C	H	N
2a	117-118	64.2	A	$C_{15}H_{12}ClNO_4S$	53.35	3.56	4.15	53.26	3.41	4.10
2c	117-118	65.5	B	$C_9H_{14}ClNO_4S$	40.39	5.24	5.24	40.20	5.10	5.40
2e	152-153	61.6	B	$C_{16}H_{12}ClNO_3S$	52.55	3.28	3.84	52.3	3.36	3.64
2f	127-128	76.7	A	$C_{11}H_{16}ClNO_4S$	44.99	5.48	4.77	44.88	5.25	4.86

A. Chloroform-petroleum ether (4:1); B. Ether-petroleum ether (9:1).

Table 2

IR, PMR and Mass Spectral Data of 2-Chlorosulfonylimino-1,3-dioxalones **2a, 2c, 2e** and **2f**

Compound No.	IR Spectra, cm^{-1} (potassium bromide) C=O	C=N	SO_2	PMR Spectra, δ (deuteriochloroform)	Mass Spectra (m/e)
2a	—	1610	1360, 1185	5.76 (s, 2H), 7.32 (s, 10H)	337 (Molecular ion), 302 (M^+-Cl)
2c	—	1595	1370, 1185	5.2 (m, 2H), 1.1-2.1 (m, 12H)	267 (Molecular ion), 232 (M^+-Cl)
2e	1690	1610	1370, 1190	7.2-8.2 (m, 10H, aromatic), 6.0 (d, 1H, J = 6 Hz, C-4H), 6.39 (d, 1H, J = 6 Hz, C-5H)	365 (Molecular ion), 265 (M^+-HSO_2Cl)
2f	—	1580	1355, 1188	5.15 (s, 2H), 1.7-2.5 (m, 8H), 1.3 (s, 3H, CH_3), 1.4 (s, 3H, CH_3)	293 (Molecular ion), 258 (M^+-Cl)

Results and Discussion.

trans-Stilbene oxide (**1a**) underwent a smooth reaction with CSI, at $-10°$ to give two products, **2a** and **3a**. The 2-chlorosulfonylimino-1,3-dioxolane derivative **2a** was isolated in pure form by fractional crystallization of the product mixture. It exhibited absorption bands in its infrared spectrum at 1610, 1185 and 1360 cm^{-1}, indicating the presence of C=N moiety and SO_2 function respectively. The analytical and other spectral (pmr and ms) data were in accordance with the assigned structure. The evidence for the *trans*-orientation of hydrogens at C-4 and C-5 comes from the hydrolysis of **2a**. A mild hydrolysis of **2a** gave *trans*-1,3-dioxolan-2-one (**4a**), known in literature [8]. Compound **4a** was further converted to the corresponding racemic diol by basic hydrolysis. The *N*-chlorosulfonyl-1,3-oxazolidin-2-one derivative **3a** could not be isolated in pure form by fractional crystallization and it underwent decomposition on column material (silica, alumina) thus making it difficult to purify by chromatography. For the same reason **3b-d** could not be isolated. The presence of **3a** in the product mixture was inferred based on the following evidences, *viz.*, the ir spectrum of the mixture showed a band located in 1790 cm^{-1} indicating the presence of an oxazolidone type of carbonyl and the hydrolysis of the above mixture yields the corresponding *N*-unsubstituted 4,5-diphenyl-1,3-oxazolidin-2-one (**5a**). The compound **5a** was proved to have *trans*-4,5-diphenyl-1,3-oxazolidin-2-one [9]. The compounds **4a** and **5a** could be obtained in yields of 72% and 23% respectively in one sequence by hydrolysing the residue left after the removal of solvent from the reaction mixture and subsequent chromatographic separation. Hydrolysis was, in general, effected by neutralizing an aqueous acetone solution of the product mixture. The reaction of *cis*-stilbene oxide (**1b**) with CSI proceeded in a similar manner. *cis*-4,5-Diphenyl-1,3-dioxolan-2-one (**4b**) and *cis*-4,5-diphenyl-1,3-oxazolidin-2-one (**5b**) were isolated after hydrolysing the initially formed products, **2b** and **3b**. From these results it is thus apparent that the reaction is stereospecific.

Likewise, cyclooctene oxide (**1c**), camphene oxide (**1f**), styrene oxide (**1d**) and chalcone epoxide (**1e**) reacted with CSI to give the expected products (Scheme 1). A simple unsymmetrical epoxide, the styrene oxide (**1d**) reacted with CSI to give 4-phenyl-1,3-dioxolan-2-one (**4d**) and 4-phenyl-1,3-oxazolidin-2-one (**5d**), after hydrolytic work-up of the reaction mixture. The fact that 5-phenyl isomer is not formed in the reaction, indicates the regiospecific nature of the reaction. Compound **5d** was fully characterized by comparing its physical and spectral characteristics with those of an authentic sample [10].

It is interesting to note that in the reaction of CSI with chalcone epoxide, the carbonyl function remains unaffected, though CSI is known to react with carbonyl compounds [11]. The tlc analysis revealed the formation of three products in this reaction. The two products appear in the first ten minute period, followed by the production of the third product within thirty minutes. A careful frac-

Table 3

1,3-Dioxolan-2-ones **4a-e** and 1,3-Oxazolidin-2-ones **5a-e** [a]

Compound No	Mp °C	Yield %	IR Spectra, cm^{-1} (potassium bromide) NH	C=O	PMR Spectra, δ (deuteriochloroform)	Mass Spectra (m/e)
4a	110-111 110-111 [8]	72.9	—	1815	7.4 (s, 10H) 5.45 (s, 2H)	240 (Molecular ion) 196 (M^+-CO_2)
4b	126-127 126 [8]	61.0	—	1790	7.0 (s, 10H) 5.95 (s, 2H)	240 (Molecular ion) 196 (M^+-CO_2)
4c	99-101	73.5	—	1805	4.4-4.9 (m, 2H) 1.1-2.2 (m, 12H)	170 (Molecular ion) 126 (M^+-CO_2)
4d	55-56 55.7-56.7 [19]	61.0	—	1770	7.7 (s, 5H) 4.6 (t, 1H) 5.0 (t, 1H) 5.8 (t, 1H)	164 (Molecular ion) 120 (M^+-CO_2)
4e	99-101	67.0	—	1820 1810 1695	7.2-8.2 (m, 10H) 5.64 (d, 1H, J = 6.3 Hz) 6.06 (d, 1H, J = 6.3 Hz)	224 (M^+-CO_2)
5a	161-162 161-162 [9]	23.0	3230	1750 1730	7.4 (s, 10H) 5.9 (bs, 1H, NH [b]) 4.7 (d, 1H, J = 7 Hz) 5.25 (d, 1H, J = 8 Hz)	239 (Molecular ion) 196 (M^+-CONH)
5b	192-193 193.5-195 [18]	22.9	3280	1745 1710	7.3 (s, 10H) 5.9 (bs, 1H, NH [b]) 4.8 (q, 2H)	239 (Molecular ion) 196 (M^+-CONH)
5c	106-107	20.5	3260 3160	1740	6.2 (bs, 1H, NH [b]) 4.4-4.9 (m, 1H)	169 (Molecular ion) 126 (M^+-CONH)
5d	138-139 137-139 [10]	30.6	3260	1730	7.5 (s, 5H) 6.0 (bs, 1H, NH [b]) 4.8-5.0 (m, 2H) 4.2 (dd, 1H, J = 7.5 Hz, 7.0 Hz)	163 (Molecular ion) 119 (M^+-CO_2)
5e	143-144	28.0	3270	1760 1725 1690	7.6-8.6 (m, 10H) 5.84 (q, 2H, J = 5.4 Hz) 6.23 (bs, 1H, NH [b])	267 (M^+) 265 (M^+-2H)

[a] All the compounds gave satisfactory elemental analyses for C, H and N. [b] Exchangeable with deuterium oxide.

tional crystallization of the product mixture led to the isolation of **2e, 3e** and **6** in pure form. The analytical and spectral (ir, pmr, ms) characteristics of **2e** and **3e** were in accordance with the assigned structure. The third component **6** was also found to be a 1:1 adduct of CSI and **1e** by its analytical and mass spectral data. Compound **6** has similar spectral characteristics (ir and ms) as that of **3e**. However the pmr spectrum of **6** exhibited a pair of doublets due to C-4 and C-5 protons at δ 6.05 and δ 6.29 with a coupling constant of 9 Hz. The AB quartet in **3e** has a J value of 4.0 Hz. This led us to the conclusion that **6** and **4e** are the corresponding *cis*- and *trans*-isomers. The value of the coupling constant is consistent with the value expected for vicinal hydrogens with *cis*- and *trans*- stereochemistry in a five membered ring [12]. The fact that the transformation of **3e** → **6** occurs, was experimentally observed by allowing an acetone solution of **4e** to stand at room temperature for an hour (tlc). On the other hand, the hydrolytic work-up of the reaction mixture within ten minutes of adding CSI (and subsequent separation by silica gel flash chromatography) led to the isolation of only two products **4e** and **5e**, in yields of 67% and 28% respectively. This shows that **2e** and **3e** are formed initially in the reaction and over a period of time **3e** gets transformed to **6**.

Dibenzoylethylene oxide (**1g**) and 4-nitrochalcone epoxide (**1h**) failed to react with CSI when, a 1:1 mixture of the two was stirred in benzene, at room temperature, for twenty-four hours. Prolonged refluxing in benzene, however, led to the formation of an unresolvable complex mixture.

Interestingly, tetraphenylethylene oxide (**1i**) reacted with CSI at 0° to produce triphenylacetophenone (**7**) in a quantitative yield, indicating the pinacolic type of rearrangement.

The above results can be rationalized by postulating the formation of a zwitterion **8** by the nucleophilic attack of the lone pair of electrons on oxygen (in epoxide), on the highly electrophilic isocyanate carbon (Scheme 2). The oxonium ion **8**, being in a strained system, is highly unstable and the epoxide C-O bond cleavage occurs to give a transient carbonium ion, which will be trapped immediately by the nucleophilic part of the zwitterion in a near concerted

manner. This explains both the regio and stereospecificity observed in the reactions. This also explains the simultaneous formation of **2** and **3** in the reaction. In the case of **1g** the nucleophilicity of the epoxide oxygen is greatly reduced by the two electron-withdrawing benzoyl groups on the adjacent carbon atoms. Moreover, an oxonium ion of type **8** is highly destabilized, because of the charge repulsion due to two benzoyl groups on the adjacent carbon atoms, and hence the formation of such an intermediate is difficult. The inert behaviour of **1h** can be explained likewise. This mechanism also explains the observed isomerization of tetraphenylethylene oxide, in the presence of CSI. The four phenyl groups prevent the cyclization of the intermediate zwitterion **9**, due to steric hindrance, and makes it susceptible to undergo a pinacol type of rearrangement, by the migration of a phenyl group. The isomerization of **3e** to **6** can be explained to be due to epimerization at C-5, by a keto-enol tautomerism, wherein enol form is stabilized by H-bonding. In contrast to the general reaction of epoxides with isocyanates, wherein oxazolidin-2-ones are formed by the isomerization of initially formed iminodioxalanes [13], the products **2** and **3** are formed by pathways shown in Scheme 2, because chlorosulfonylimino-1,3-dioxalanes when subjected to the same reaction conditions did not show any isomerization.

Scheme 2

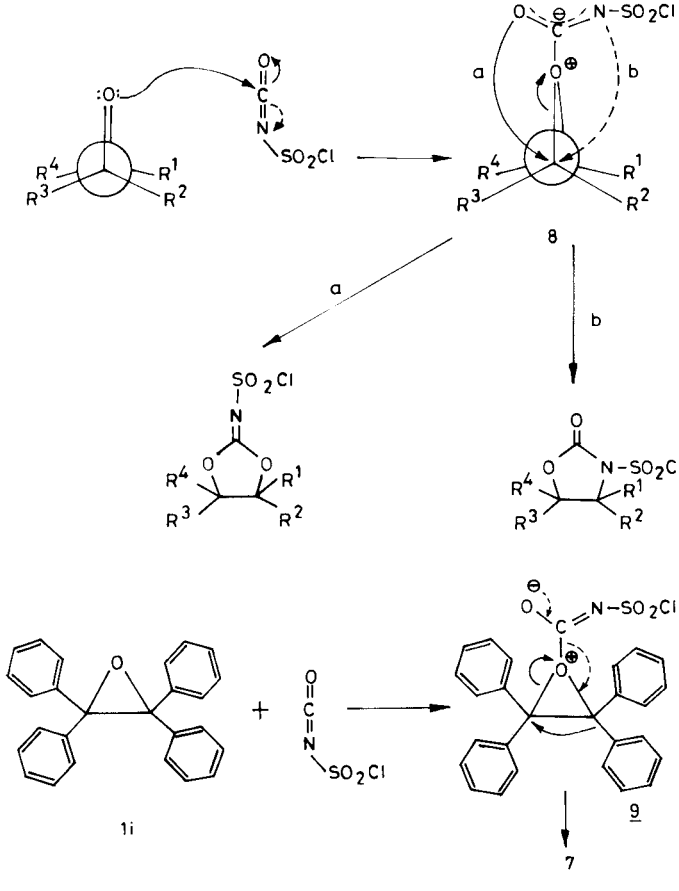


Table 4

Analytical Data of 1,3-Dioxalan-2-ones **4a-e** and 1,3-Oxazolidin-2-ones **5a-e**

Compound No.	Molecular Formula	C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
4a	$C_{15}H_{12}O_3$	75.0	75.1	5.0	5.15	—	—
4b	$C_{15}H_{12}O_3$	75.0	74.9	5.0	5.12	—	—
4c	$C_9H_{14}O_3$	63.53	63.30	8.23	8.32	—	—
4d	$C_9H_8O_3$	65.85	65.73	4.88	4.95	—	—
4e	$C_{16}H_{12}O_4$	71.64	71.52	4.48	4.61	—	—
5a	$C_{15}H_{13}NO_2$	75.31	75.20	5.44	5.26	5.85	5.90
5b	$C_{15}H_{13}NO_2$	75.31	75.40	5.44	5.35	5.85	5.92
5c	$C_9H_{15}NO_2$	63.90	63.71	8.87	8.60	8.28	8.35
5d	$C_9H_9NO_2$	66.26	66.10	5.52	5.32	8.59	8.65
5e	$C_{16}H_{13}NO_3$	71.90	71.78	4.87	4.62	5.24	5.35

The yields of cyclic carbonates obtained in the reaction sequence described above are reasonably good (61-74%, see Table 3) and the method of isolation is simple. Hence the reaction can be of potential synthetic value, as it provides a one-pot synthesis of protected 1,2-diols from epoxides. The available methods [14-16] for the conversion of epoxides to cyclic carbonates are limited and have not been applied to more substituted and keto epoxides, hence the generality of the reaction has not been established. In the present study the reaction seems to be of general nature except for the sterically crowded epoxides and the epoxides containing electron withdrawing substituents at C-2 and C-3. Thus with limited exceptions this method can serve as a simple one-pot method, for the conversion of epoxides to cyclic carbonates.

EXPERIMENTAL

All melting points are uncorrected and were taken on a Fisher-Johns melting point apparatus. The ir spectra were recorded on Perkin-Elmer Model-580 or Model-377 infrared spectrophotometers. The pmr spectra were recorded on Brucker WP-80 (80 MHz) or Varian EM-390 (90 MHz) spectrometers. Chemical shifts are reported in parts per million downfield from internal reference TMS (δ). Multiplicity is indicated using the following abbreviations: s (singlet), bs (broad singlet), d (doublet), t (triplet) and q (quartet). Mass spectra were recorded on a Jeol JMS-300D mass spectrometer at 70 eV. The elemental analyses were carried out in Coleman automatic carbon, hydrogen and nitrogen analysers.

Starting Materials.

CSI was purchased from Fluka AG, Switzerland and was used as such. Epoxides were prepared from the corresponding olefins by the known methods [17] using perbenzoic acid/mCPBA/hydrogen peroxide-base, and were purified either by crystallization or by distillation.

Reaction of **1a** with CSI.

A solution of CSI (0.28 ml, 0.003 mole) in dry benzene-dichloromethane mixture (5.1, 10 ml) was added dropwise, at −10° to a magnetically stirred solution of **1a** (0.590 g, 0.003 mole) in the same solvent mixture (10 ml). The reaction was monitored by tlc. After ten minutes the reaction mixture was poured into water and the organic layer was separated. It was washed with water, dried over anhydrous sodium sulfate and the solvent was evaporated at room temperature. The residual oil [A] was taken up in chloroform and petroleum ether was added dropwise until the

solution became slightly turbid, and cooled in a refrigerator, when colorless crystals of **2a** separated [*]. Solvent was evaporated from this filtrate to obtain an oil. This was dissolved in 20 ml of acetone-water mixture (95:5) and the resulting acidic solution was neutralized by dropwise addition of 5% aqueous potassium hydroxide solution. The solution was stirred for thirty minutes and diluted with water. This aqueous mixture was extracted with ether (3 × 20 ml), the combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate, and the solvent evaporated off. The resulting residue was dissolved in a mixture of chloroform-petroleum ether (3:1). The solution on cooling furnished colorless crystals of **5a** (yield 0.15 g, 20%).

[*] Compounds **2c**, **2e**, and **2f** were prepared using a similar procedure. The yield, mp, analytical and spectral data of **2a**, **2c**, **2e** and **2f** are collected in Tables 1 and 2.

The residual oil **A** when subjected to hydrolytic work up as described above gives two products **4a** and **5a**. The components were separated in pure form, from the product mixture by flash chromatography (silica gel, tlc grade, eluant: ether-petroleum ether; 20:80 and 60:40). A similar procedure was adopted in the reaction of **1b-e** with CSI and products **4b-e** and **5b-e** were isolated. The yield, mp, and spectral data are given in Table 3.

Hydrolysis of **2a**.

Hydrolysis of **2a** (0.170 g, 0.0005 mole) in a similar manner as described above furnished **4a**, which was crystallized from ether-petroleum ether (4:1), yield 0.115 g, 95%, mp 110-111°, lit [8] mp 110-111°.

Likewise the hydrolysis of **2c** and **2e** furnished **4c** and **4e** in yields of 88% and 90% respectively.

Reaction of **1e** with CSI.

To a magnetically stirred solution of **1e** (0.450 g, 0.002 mole) in dry benzene-dichloromethane mixture (4:1, 10 ml) at −15° was added dropwise a solution of CSI (0.18 ml, 0.002 mole) in the same solvent (5 ml). The work-up of the reaction mixture after 30 minutes in the usual manner, furnished an oil which was subjected to fractional crystalliztion at room temperature (~15°) using ether-petroleum ether and dichloromethane-petroleum ether as solvents. This yielded three compounds **2e**, **3e** and **6** in pure form.

trans-N-Chlorosulfonyl-4-phenyl-5-benzoyl-1,3-oxazolidin-2-one (**3e**).

This compound was obtained in a yield of 12% (0.09 g), mp 139-140°; ir (potassium bromide): 1820, 1810, 1690 (CO), 1375, 1160 (SO_2), 1080 cm^{-1}; pmr (deuteriochloroform): δ 7.1-7.9 (m, 10H, aromatic), 5.56 (d, 1H, J = 4 Hz, C-4H), 5.62 (d, 1H, J = 4 Hz, C-5H); ms: (70 eV) m/e 365 (molecular ion), 330 (M^+-Cl), 266 (M^+-SO_2Cl).

Anal. Calcd. for $C_{16}H_{12}ClNO_5S$: C, 52.60; H, 3.29; N, 3.83. Found: C, 52.72; H, 3.38; N, 3.69.

cis-N-Chlorosulfonyl-4-phenyl-5-benzolyl-1,3-oxazolidin-2-one (**6**).

This compound was obtained in a yield of 4% (0.08 g), mp 158-159°; ir (potassium bromide): 1820, 1810, 1690 (CO), 1340, 1170 (SO_2) cm^{-1}; pmr (deuteriochloroform): δ 7.1-7.5 (m, 10H, aromatic), 6.29 (d, 1H, J = 9.0 Hz, C-5H), 6.05 (d, 1H, J = 9.0 Hz, C-4H); ms: (70 eV) m/e 365 (molecular ion), 330 (M^+-Cl), 266 (M^+-SO_2Cl).

Triphenylacetophenone (**7**).

The reaction of **1i** (0.695 g, 0.002 mole) and CSI (0.18 ml, 0.002 mole) was carried out in an analogous manner, described above, at 0°. The compound **7** was isolated after the usual work-up. Compound **7** was found to be identical in all respects (physical and spectral characteristics) with that of an authentic sample prepared from benzpinacol rearrangement, yield 0.695 g, 100% mp 181-182°, mixed mp 181-182°; ir (potassium bromide): 1670 (CO) cm^{-1}.

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