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Kinetic Studies on the Chemical and Electrochemical Reduction of Some 4-Arylidene-5-pyrazolone Compounds

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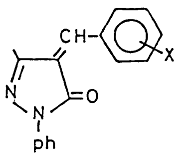
Kinetics of chemical and electrochemical reduction of some 4-arylidene-5-pyrazolones were studied. The chemical reduction was performed using aluminum hydride. The electrochemical reduction in 0.1 mol dm^{-3} TEAP/DMF was studied by cyclic and convolution potential sweep voltammetry at HDME. The title compounds exhibit two diffusion-controlled irreversible mono electronic cv waves. Both waves follow EC kinetics and they are attributed to the reduction of the pyrazolin carbonyl group. The kinetics of the chemical and electrochemical reduction were proposed and discussed in terms of the molecular structure of the subject arylidenes.

Though many investigations have been reported concerning the synthesis of arylidenes,[1] dyes[2,3] and electronic absorption spectra of arylidenepyrazolones,[4] scarcely attention has been paid to chemical and electrochemical reduction of such compounds.[5] It was found that the polarographic half-wave potentials of some 4-(4-substituted arylidene)-5-pyrazolones correlate with the Hammett's constant. Kinetics of the chemical and electrochemical reduction of the title compounds were not yet studied.

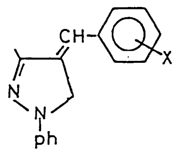
In continuation of our work[6] an investigation of the chemical and electrochemical reduction mechanism of a series of 4-(4-substituted arylidene)-5-pyrazolones is carried out. Herein, chemical and cyclic and convolution potential sweep voltammetric results are reported and discussed in terms of the molecular structure of the subject arylidenepyrazolones.

Experimental

a) Synthesis of 4-Arylidene-5-pyrazolones. 1-Phenyl-3-methyl-4-arylidene-5-pyrazolones were synthesized and purified as described before.[7] The subject compounds are:



a$_{1-3}$



b$_{1-3}$

1, X=H, **2**, X=OCH_3, **3**, X=Br

Stock solution (1.0×10^{-2} mol dm^{-3}) of arylidenepyrazolone was prepared in the supporting electrolyte (0.1 mol dm^{-3} TEAP/DMF).

b) Synthesis of Aluminum Hydride (alane). To a cooled stirring solution of lithium aluminum hydride, $LiAlH_4$, 0.12g (3.0 mmol) in 20.0 ml dry ether was added, 0.12 g (1.0 mmol) of anhydrous aluminum chloride, $AlCl_3$, in portions to give stoichiometrically required amount of AlH_3. The mixture was stirred at room temperature until $AlCl_3$ dissolved and LiCl was completely precipitated.

$$3\ LiAlH_4 + AlCl_3 \rightarrow 3\ LiCl + 4\ AlH_3 \qquad (1)$$

c) Selective Reduction of Arylidenepyrazolones with alane. (General Procedure). 20.0 ml etheral solution of AlH_3[8] was added to a stirring solution of the pyrazolone derivative (2.0 mmol) in dry ether. The reaction mixture was refluxed under dry conditions (6—7 h). The excess hydride was decomposed by addition of dilute HCl then the reductive product was extracted with ether and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave a viscous residue which after grunding with petroleum ether solidifies as colored solid. The products were crystallized from acetone. The arylidenepyrazolones subjected for the selective chemical reduction are: **2a**, **3a**, and 1-phenyl-3,4,4-trimethyl-5-pyrazolone (**4a**). Experimental data of all the isolated products were summarized in Table 1.

Tetraethylammonium perchlorate, TEAP, (Fluka), and *N,N*-dimethylformamide (A.R. grade DMF) were purified as described earlier.[6,9]

d) Controlled Potential Coulometric Measurements. Controlled potential coulometric electrolyses were performed at the peak current potential of the two cv waves. Coulometric measurements were conducted in 1.0×10^{-3} mol dm^{-3} solu-

Table 1. Experimental Data for the Reductive Arylidenepyrazolone Products

Comp No.	Formula	Reaction time h	Yield %	Mp °C	Analysis (calcd/found) C%	H%	N%
2b	$C_{18}H_{18}N_2O$	6.5	50	118	77.69	6.47	10.07
					77.49	6.52	9.80
3b	$C_{17}H_{15}N_2Br$	6.0	84	135	59.82	4.39	8.21
					59.98	4.55	8.13
4b	$C_{12}H_{16}N_2$	7.0	22	140	76.95	8.51	14.89
					76.50	8.70	14.75

tions. The cell was continuously flushed with nitrogen and the analysis was continued until the current had decayed to the background level. Completion of the electrolysis was confirmed by cv measurements.

e) Instrumentations. An EG&G PAR model SMDE 303 mercury drop system of small hanging-drop mode was used as HDME working electrode at 298 K. The electrode area was 1.83×10^{-3} cm^2. The counter electrode was platinum wire. Silver/silver ion (0.01 mol dm^{-3} $AgNO_3$ in 0.1 mol dm^{-3} TEAP/DMF) electrode was used as a reference electrode throughout. All solutions were purged with pure nitrogen.

An EG&G PAR model 173 Potentiostat/Galvanostat with positive feedback IR compensation and EG&G PAR model 175 Universal programmer function generator were used for the cyclic voltammetric measurements. The cyclic voltammograms were recorded on PAR model RE 0091 X–Y recorder.

Controlled potential coulometry was carried out with EG&G PAR model 179 Digital Coulometer and PAR model 337A Coulometric cell system.

Electrochemical data were performed using an AMSTRAD personal computer PC 1512.

Spectrophotometric measurements (IR and ^{1}H NMR spectra) were performed on a Perkin-Elmer 137 IR Spectrophotometer in KBr and Varian A-60 ^{1}H NMR Spectrophotometer at 60 MHz.

Results and Discussion

i) Cyclic Voltammetry. Two cyclic voltammetric reduction waves are observed for all the 1-phenyl-3-methyl-4-arylidene-2-pyrazolin-5-ones (4.98×10^{-4} mol dm^{-3}) in 0.1 mol dm^{-3} tetraethylammonium perchlorate/dimethylformamide (TEAP/DMF) at hanging dropping mercury electrode. The cyclic voltammetric data obtained are given in Table 2. The cv waves appear to be irreversible, their anodic counterparts are lacking at all scan rates explored.

The potential width measured by ($E_p-E_{p/2}$) for the two cv waves are larger than the values expected for a mono-electronic charge-transfer reversible processes (56.5/n mV at 298 K) (c.f. Table 2).[10,11] The peak potential of the two cv waves does shift to more negative potentials on increasing the scan rate, to the extent of 30.0±0.3 and 35±0.2 mV for the tenfold increase in scan rate for the first and second cv waves, respectively. This reveals that, the cv waves are due to a reversible one electron-transfer process coupled with an irreversible first-order follow-up chemical reaction. The chemical reaction is suggested to be protonation.

The peak current, i_p of both cv waves correlates significantly with $\nu^{1/2}$, (r=0.998) and concentration of the depolarizer as well (r=0.999). This evidences that the two cv waves are diffusion-controlled[10] with no adsorption complications.

On comparing i_p–$\nu^{1/2}$ relations with the diagnostic criteria for EC mechanism presented earlier,[10] the diffusion coefficient, D, for the subject arylidenepyrazolones are computed. The data obtained are collected in Table 2.

According to Nicholson and Shain,[10] an excellent agreement between the experimental and calculated peak width ($E_p-E_{p/2}$) is seen. This provides completing evidence that the cv waves follow solely the $E_{rev}C_{irr}$ mechanism. Furthermore, the first-order rate constants of the follow-up irreversible protonation reaction, k_c, are estimated. Moreover, the polarographic half-wave and the formal electrode potentials, if one considers that $D_R=D_O$ (the diffusion coefficients of the reduced and oxidized forms, respectively) are determined using Eqs. 2 and 3.[10]

$$E_p = E_{1/2} - 0.780\,(RT/nF) + RT/2nF \ln \lambda, \qquad (2)$$

where $\lambda = k_c(RT/nF)\nu$.

$$E_{1/2} = E^\circ + (RT/nF) \ln \sqrt{(D_R/D_O)}. \qquad (3)$$

The computed values of E° and k_c are depicted in Table 2.

Table 2. Cyclic Voltammetric Data for 4.98×10^{-3} mol dm^{-3} 4-Arylidene-5-pyrazolones in 0.1 mol dm^{-3} TEAP/DMF (1st wave)

No.	Scan rate	$-E_p^{a)}$	$E_p-E_{p/2}$	$i_p/\nu^{1/2}$	$10^7D^{c)}$	$-E^\circ/E_{1/2}^{d)}$	$k_c^{e)}$
	mV s^{-1}		mV	b)	cm^2 s^{-1}	V	s^{-1}
2a	20	1.600	55	6.220	5.45	1.423	0.196
	50	1.615	57	6.44			
	100	1.625	60	6.32			
	200	1.633	61	6.13			
	500	1.640	60	5.71			
1a	20	1.480	60	7.14	6.89	1.310	0.248
	50	1.495	60	7.42			
	100	1.505	65	7.21			
	200	1.515	67	6.79			
	500	1.523	66	6.65			
3a	20	1.400	60	6.79	6.36	1.228	0.229
	50	1.410	60	6.44			
	100	1.420	60	6.76			
	200	1.430	57	6.71			
	500	1.440	63	6.28			

a) ±2.1%. b) in $\mu A(V^{-1}\,s)^{-1/2}$. c) ±3.2%. d) ±2.5%. e) ±3.5%.

On the other hand, a further verification that the substrate reduces electrochemically via an $E_{\mathrm{rev}}C_{\mathrm{irr}}$ mechanism is revealed from the slightly decrease in the current function with increasing the scan rate (c.f. Table 2).

The number of electrons involved along the two cv waves is determined on controlling the potential at their peak current potentials. It is found that 1.1 and 0.9 moles of electrons per mole of the arylidenepyrazolone are consumed for electrochemical reduction of the first and second cv waves, respectively. Thus, the number of electrons transferred is one for both cv waves. Similar behavior is seen with the other arylidenepyrazolones under investigation.

ii) Convolution Sweep Voltammetry. Analysis of cyclic voltammetric data has a disadvantage that the potential dependent rate law must be selected before the treatment of data. However, convolution technique allows this disadvantage to be overcome. This is made by convolution of the current with the function $(\pi t)^{1/2}$ and data are processed in terms of both current and convoluted current. It is no longer necessary, under this conditions, to (a priori) state the charge transfer rate law which is instead obtained as a result of the treatment of data[12—16].

Examination of the cyclic voltammetric convoluted data for the 4-arylidenepyrazolones in the scan rate range of 20—500 mV s^{-1} reveals that they electrochemically reduce irreversibly. This is established from the feature of the cyclic convoluted current voltammogram, since the convoluted current, I, neither returns to its initial (zero) value nor superimposes during the reverse half of the sweep with I on the forward sweep regardless of the scan rate. Figure 1 illustrates the cyclic original and convoluted voltammograms for the first cv wave for **1a** at scan rate of 200 mV s^{-1} as a representative example.

The logarithmic analysis of the convoluted data is used to established the mechanism of the electrochemical reduction process. The analysis is tested for the various reaction mechanisms (E_{rev}, E_{irr}, CE, ECE, ...etc). In the entire range of scan rate, the data fit satisfactorily the following equation for all the subject pyrazolones:

$$E = E^{\circ} + (RT/2nF)\ln k_c + (RT/nF)\ln[(I_l - I)/i], \quad (4)$$

where I is the convoluted current, i is the original current, $I_l = nFAC_{\mathrm{O}}D^{1/2}$ is the limit of I as E approaches infinity and the remaining symbols have their usual significances. They give rise straight lines with slope values close to the theoretical value (59.1/n mV at 298 K for decimal logarithm) for an $E_{\mathrm{rev}}C_{\mathrm{irr}}$ mechanism. The regression line obtained for the first cv wave of **1a** as a representative example can be represented by Eq. 5. The linearity and the location of the obtained straight line on the potential axis do not depend on the sweep rate. This behavior verifies the above conclusion that the electrochemical reduction of the subject pyrazolones take place via an $E_{\mathrm{rev}}C_{\mathrm{irr}}$ kinetics.

$$E = -(1.445 \pm 0.005) + (61.1 \pm 1.1) \times 10^{-3}\log[(I_l - I)/i]$$
$$r = 0.998 \quad (5)$$

From Eqs. 4 and 5 the formal electrode potential, E°, for the subject arylidenepyrazolones are computed. The results obtained depicted in Table 1. It is clear that these values are in good agreement, within the experimental error limits, with those obtained from the above cyclic voltammetric data.

iii) Chemical Reduction: Special attention is paid to the selective reduction suitable for the reduction of the carbonyl group without reduction of the arylidene group of the subject arylidenepyrazolones.

The most common reducing agents are the metal hydrides and hydrogenation catalysts. The reagents used in the reduction by hydride transfer (metal hydrides)[17] are two types. They are nucleophilic substances such as lithium aluminum hydride (LAH) and sodium borohydride, as well as the electrophilic species diborane, aluminum hydride (alane) and derivative thereof.[18,19]

Lithium aluminum hydride often reduces the α,β-unsaturated ketones.[20,21] The double bond reduction is avoided by the use of aluminum hydride, which selectively reduces the carbonyl group only.

The selective reduction of **2a**—**4a** is carried out using aluminum hydride. The reduction process was followed by ^{1}H NMR spectra, which show a shift in the vinylic proton resonance to a higher magnetic field.

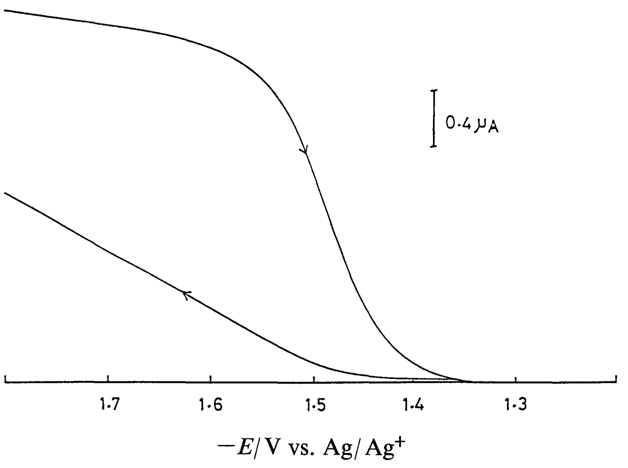


Fig. 1. Convolution voltammogram for the first cv wave of the reduction of 4-arylidenepyrazolone, **1a**, at scan rate of 200 mV s^{-1}.

Table 3. IR Spectroscopic Data (KBr, cm^{-1})

Compd	νC=O	νC=N	νC=C Exocyclic
2a	1670	1630	1610
2b	—	1625	1610
3a	1670	1630	1610
3b	—	1630	1590
4a	1685	1620	—
4b	—	1625	—

Table 4. ^{1}H NMR Spectra δ (DMSO)/ppm

Compd	=CH	Arom. proton	OCH_3	$-CH_2$	$-CH_3$
2a	8.8 (s, 1H)	7.1—8.2 (m, 9H)	3.9 (s, 3H)	—	2.4 (s, 3H)
2b	8.3 (br, 1H)	6.8—8.2 (m, 9H)	3.8 (s, 3H)	3.6 (s, 2H)	2.3 (s, 3H)
3a	8.3 (s, 1H)	7.1—8.0 (m, 9H)	—	—	2.2 (s, 3H)
3b	8.1 (br, 1H)	6.7—7.9 (m, 9H)	—	3.9 (s, 2H)	2.2 (s, 3H)
4a	—	7.8—7.2 (m, 9H)	—	—	2.6 (s, 3H); 2.45 (s, 6H)
4b	—	7.8—7.4 (m, 9H)	—	4.2 (br, 2H)	2.2 (s, 3H); 1.2 (d, 3H); 1.2 (s, 3H)

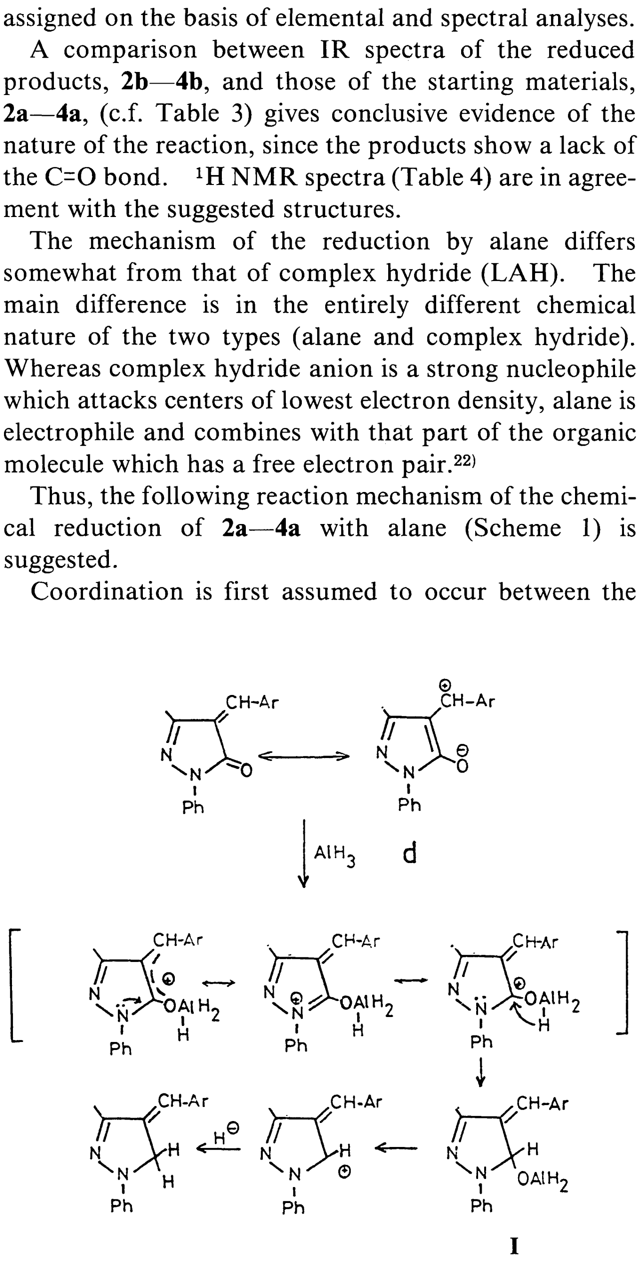
This is attributed to the disappearance of deshielding effect of the carbonyl group. Moreover, new singlet signals are developed due to the appearance of methylene group. The structure of the isolated products are assigned on the basis of elemental and spectral analyses.

A comparison between IR spectra of the reduced products, **2b**—**4b**, and those of the starting materials, **2a**—**4a**, (c.f. Table 3) gives conclusive evidence of the nature of the reaction, since the products show a lack of the C=O bond. ^{1}H NMR spectra (Table 4) are in agreement with the suggested structures.

The mechanism of the reduction by alane differs somewhat from that of complex hydride (LAH). The main difference is in the entirely different chemical nature of the two types (alane and complex hydride). Whereas complex hydride anion is a strong nucleophile which attacks centers of lowest electron density, alane is electrophile and combines with that part of the organic molecule which has a free electron pair.[22)]

Thus, the following reaction mechanism of the chemical reduction of **2a**—**4a** with alane (Scheme 1) is suggested.

Coordination is first assumed to occur between the carbonyl oxygen atom and alane. Intramolecular hydride transfer is possible in the complex and intermediate (**I**) still contains hydrogen atom directly attached to the aluminum atom. The intermediate heterolyses by loosing an aluminate ion, a good leaving group, to give carbonium ions which are reduced to methylene group leading to the final product.



Scheme 1.

From the foregoing results it can be deduced that:

1) $AlCl_3$ is added to reduce the reduction tendency power of $LiAlH_4$ and consequently produces a reagent more specific for the particular reaction as described by elsewhere.[18)]

2) The arylidene substituents play a role in the stabilization of the dipolar form **d** (Scheme 1). Introduction of an electron-withdrawing group in the *p*-position of the arylidene moiety increases the facility of the reduction.

Kinetics of the Electrochemical Reduction. Electrochemical reduction kinetics of 1-phenyl-3-methyl-4-arylidene-2-pyrazolin-5-ones in 0.1 TEAP/DMF at 298 K, the electrode reaction mechanism are discussed on the basis of the above results. They are electrochemically reduced via two irreversible diffusion-controlled single-electronic cv waves. These cv waves follow an $E_{rev}C_{irr}$ kinetics.

The subject arylidenepyrazolones have three possible reduction sites, the azomethine, -CH=N, of the pyrazolone nucleus, the cyclic carbonyl, C=O, and the exocyclic arylidene =CH-Ar, groups. The endocyclic -CH=N- group requires high energy for reduction. Therefore, the two other sites are susceptible for reduction.

To establish the site of reduction in the subject substrates, they are subjected to selective chemical reduction for the carbonyl group and then are tested voltammetrically. The reduced products show no cv waves. This is ascribed to the lacking of their 5-carbonyl group. Thus, the electrochemical reduction site is most likely the 5-carbonyl group, while the arylidene group is electroinactive at such circumstances.

The kinetics of the electrochemical reduction of the 4-arylidene-5-pyrazolones is proposed and discussed as follows:

The first irreversible mono-electronic reduction wave is due to reversible addition of an electron to the pyrazolone molecule and can be represented by reaction (6). Simple charge-transfer reaction (6) does not, however, justify the irreversibility of the first wave and other step must be invoked to rationalize the data obtained. Taking into account that the first cv wave proceeds via an $E_{\mathrm{rev}}C_{\mathrm{irr}}$ mechanism and the reduction of carbonyl group consumes at least two electrons and two protons, an irreversible first-order protonation reaction (7) is assumed to be taken place. At more negative potentials, further electron is reversibly added to the radical $\mathrm{ArpyH}^{\bullet}$, according to reaction (8). Another irreversible first-order proton addition, reaction (9), to the ArpyH^{-} anion takes place to the final product. Occurrence of reactions (7) and (9) can justify the irreversibility of the two cv waves.

$$\mathrm{Arpy} + \mathrm{e} \neq \mathrm{Arpy}^{\overline{\bullet}} \tag{6}$$

$$\mathrm{Arpy}^{\overline{\bullet}} + \mathrm{H}^{+} \xrightarrow{k_{\mathrm{c}}} \mathrm{ArpH}^{\bullet} \tag{7}$$

$$\mathrm{Arpy}^{\bullet} + \mathrm{e} \neq \mathrm{ArpyH}^{-} \tag{8}$$

$$\mathrm{ArpyH}^{\overline{\bullet}} + \mathrm{H}^{+} \xrightarrow{k_{\mathrm{c}}} \mathrm{ArpH}_{2} \tag{9}$$

Structural Effects. From the examination of the data obtained (cf. Table 2), it is evident that the influence of the para substituents in the 4-arylidene moiety on the electrochemical reduction (expressed in the values of the peak current potential, E_{p}) is as expected. The *p*-methoxy substituted derivative exhibits the most negative shift of E_{p}, whereas the *p*-bromo one shows a positive shift compared to the parent unsubstituted arylidenepyrazolone **1a**. This is explained as follows. On introduction of electron-donating group (methoxyl group) in the arylidene phenyl moiety, an increase in the electron density of the carbonyl group is expected. Consequently, the electrochemical reduction of the carbonyl group becomes more difficult. This appears as a shift in E_{p} to more negative potentials. On the other hand, introduction of electron-withdrawing group (bromo) reduces the electron density on the carbonyl center. This in turn makes the electrochemical reduction easier and appears as a positive shift in E_{p}.

The substituent effect is expressed quantitatively by the relation between the peak current potential of the arylidenepyrazolones and the Hammett's substituent constants, σ_{p}^{-}. It is evident that, the peak potentials for the first cv wave correlate with the σ_{p}^{-} Hammett constants. The best linear least-square line obtained is represented as follows:

$$E_{\mathrm{p}} = (0.218 \pm 0.002)\,\sigma_{\mathrm{p}}^{-} - (1.463 \pm 0.013) \quad r = 0.983(10) \tag{10}$$

This confirms that the electrochemical reduction of the subject arylidenepyrazolones follow the same mechanism for all the compounds under investigation. On the other hand, the reaction constant ρ obtained is 218 mV comparable to those of substituted benzaldehyde (310 mV), benzophenone oximes (300 mV) and azomethine (300 mV) etc.[23] These are interpreted on the basis as the arylidene moiety becomes a structure completely coplanar with the rest of the molecular plane. Also, this verifies strongly that the electrochemical reduction center is the α,β-unsaturated 5-carbonyl group.

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