NMR of Terminal Oxygen. Part 10.[1] ^{17}O NMR Spectra of Carbonyl Phosphonium Ylides and Diazocarbonyl Compounds: Resonance Stabilization, Bond Order and Excitation Energy

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On the scale of carbonyl electrophilicities, measured by ^{17}O NMR spectroscopy, carbonyl groups in aroyl (**1**), acetyl (**2**) and ethoxycarbonyl (**3**) phosphonium ylides are similar to those of amide groups, showing a considerable effect of resonance donation. The relative weight of the limiting formulae in the resonance in **1** and **3** is found to be close to earlier estimations which were based upon ^{1}H and ^{13}C NMR shift values. For comparison, a series of phenacyl compounds $PhCOCH_2X$ have been investigated; they show a very small effect of X on δ_0 The δ_0 values of aroyl (**4**) and ethoxycarbonyl (**5**) diazoalkanes are found to be less shielded than those of the corresponding ylides, demonstrating the importance of long-wave electronic transitions observable in the UV–VIS spectrum. However, the substituent sensitivity coefficient ρ^+ of aroyldiazoalkanes **4** is similar to those of esters and amides.

In carbonyl phosphonium ylides **B** (= α-carbonyl methylenephosphoranes A) the carbanion is stabilized by resonance with the carbonyl group (mainly $\mathbf{B} \longleftrightarrow \mathbf{C}$;[2,3] ^{13}C and ^{1}H NMR spectra show that formula **A** is of little importance[4]); by the same electron displacement the carbon atom of the carbonyl group loses part of its electrophilic activity, as in other cases of carbonyl resonance. In amides,[5] esters[5] and carbonyl ylides[6] the resonance energies, estimated or measured by the height of the rotational barriers, are rather similar, *ca.* 15 kcal mol^{-1}.‡ Chemical data, too, point to a low level of electrophilicity of the carbonyl group: carbonyl ylides are hydrolysed only on prolonged heating, similar to amides.[2] However, carbonyl stretch vibrations at *ca.* 1530 cm^{-1},[7,8] and C–O bond length data[2] do not agree with this estimation; they seem to indicate a still higher polarization of the carbonyl bond.

$$\underset{\mathbf{A}}{\text{R–CO–CH=PR}_3} \longleftrightarrow \underset{\mathbf{B}}{\text{R–CO–CH}^-\text{–PR}_3{}^+} \longleftrightarrow \underset{\mathbf{C}}{\text{R–C(O}^-\text{)=CH–PR}_3{}^+}$$

Diazocarbonyl compounds **D** can also be considered as acyl-stabilized ylides **E**:[9]

$$\underset{\mathbf{D}}{\text{R–CO–CH=N}^+\text{=N}^-} \longleftrightarrow \underset{\mathbf{E}}{\text{R–CO–CH}^-\text{–N}^+\text{≡N}} \longleftrightarrow \underset{\mathbf{F}}{\text{R–C(O}^-\text{)=CH–N}^+\text{≡N}}$$

The chemical properties show that these compounds have somewhat less carbanion character than carbonyl ylides; IR[10] and bond length data,[11] and rotational barriers,[12] point to C=O characteristics similar to those of amides. As a general comparison of the resonance of C, N and O nucleophiles with carbonyl groups is interesting, clearly more data are required.

We have recently shown[13,14] that ^{17}O NMR (in contrast to ^{13}C NMR) spectroscopy, is particularly useful in characterizing the electronic state of carbonyl groups, including their electrophilicity. In the presence of resonance effects, which diminish the electrophilicity of the group and increase the electron density around the oxygen atom, the latter is considerably more shielded (see Fig. 1). It is true that, in principle, shift values depend not only upon bond order, but are influenced also by other factors (see below); for several important carbonyl functions, however, it has been demonstrated by NQR measurements[15] that the influence of the bond order (related to the electrophilicity of the group) is predominant in determining the δ_O values. To confirm this, the 'tool of increasing electron demand' developed[16] to characterize carbenium ion centres, was applied to carbonyl compounds.[13] In this case the 'tool' implies that the less the electron deficiency of a carbonyl group –CO–X is diminished by resonance donation from X, the more any (spectral or other) carbonyl property will be sensitive to other substituents, notably electron donor and acceptor substituents Y in the arene ring of p-YC_6H_4COX. The ^{17}O shift values are particularly appropriate for application of the 'tool'. The arene substituent sensitivity, as usual measured by the Hammett-Brown coefficient ρ^+, varies considerably from one group COX to another. In the absence of n-donation, as in benzaldehydes and acetophenones, $\rho^+ = 26$ and 22 respectively; it is 29 for the still more electron-demanding ω,ω,ω-trifluoroacetophenones.[13] In the presence of electron donating groups, which diminish the electron demand of the carbonyl group, the substituent sensitivity ρ^+ is lowered: –COCl, 20; –COF, 14; $-CO_2Me$, 8; $-CONH_2$, 7; $-CO_2{}^-$, 5.[13] The ρ^+ values thus parallel the chemical electrophilicities of the carbonyl groups, which are qualitatively very well known from chemical reactivities, but which had not before been classified numerically. For the most important carbonyl functions, *i.e.* those in which the atom directly bound to the carbonyl carbon belongs to a second row element (C, N, O, F), a reasonably good correlation (r = 0.970) between shift values δ_O and substituent sensitivities ρ^+ has been found (see Fig. 1);[13,14] this allows one to use either scale to estimate the relative electrophilicity of carbonyl groups. In order to situate carbonyl phosphonium ylides and diazocarbonyl compounds on this scale of carbonyl electrophilicity, we have measured their ^{17}O shift values, and, for diazocarbonyl compounds, their substituent sensitivity ρ^+.

Results

The phenacyltrimethylphosphonium ylides **1a–c** show signals at δ_O *ca.* 320 (Table 1), not far from the values of benzamide (326 ppm[13]) and methyl benzoate (337 ppm[13]), and much more shielded than those of acetophenone (549 ppm[17]); this corresponds to the resonance-reduced electrophilicity of the carbonyl group in **1**. A similar relationship is found for the

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‡ 1 cal. = 4.184 J.

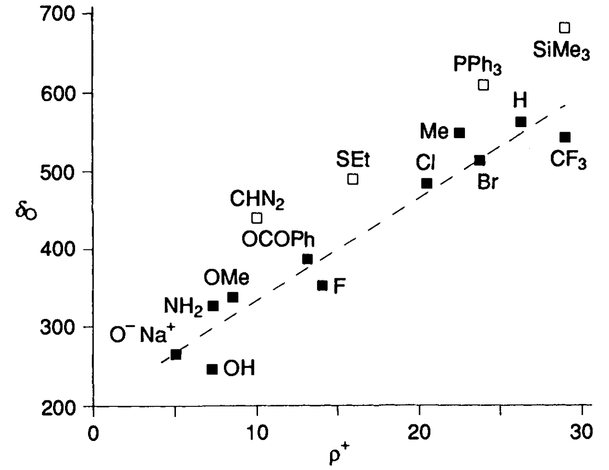

Fig. 1 Plot of the chemical shift values δ_O of benzoyl compounds PhCOX *vs.* the substituent sensitivity ρ^+ of ArCOX. The correlation line has been drawn for the data points marked by ■.

Table 1 ^{17}O NMR chemical shift of carbonyl phosphonium ylides (**1–3**) and carbonyl diazoalkanes (**4**, **5**)

Compound	δ_O	w[a]	λ/nm	ε/dm^3 mol^{-1} cm^{-1}
1a PhCO-CHPMe$_3$	327.4	240	328	10 200[b]
1b *p*-MeOC$_6$H$_4$CO-CHPMe$_3$	314.8[c]	690		
1c *p*-NO$_2$C$_6$H$_4$CO-CHPMe$_3$	323.9[d]	430		
2 MeCO-CHPPh$_3$[e]	373.2	650	295	4 400
3 EtOCO-CHPPh$_3$	271.5[f]	330	288	3 100
4a PhCO-CHN$_2$	439.9	170	400	25
4b *p*-MeOC$_6$H$_4$CO-CHN$_2$	430.3[g]	340		
4c *p*-MeC$_6$H$_4$CO-CHN$_2$	436.8	240		
4d *p*-FC$_6$H$_4$CO-CHN$_2$	437.1	210		
4e *p*-BrC$_6$H$_4$CO-CHN$_2$	439.1	250		
4f *p*-CF$_3$C$_6$H$_4$CO-CHN$_2$	444.4	280		
4g *p*-CNC$_6$H$_4$CO-CHN$_2$	444.9	330		
4h *p*-NO$_2$C$_6$H$_4$CO-CHN$_2$	447.1[h]	330		
5 EtOCO-CHN$_2$	320.8[i]	120	389	14

[a] Line-width at half height, in Hz (after deduction of 100 Hz line-broadening). [b] For $-$PPh$_3$. [c] MeO; 53.1 (660 Hz). [d] NO$_2$; 571.8 (830 Hz). [e] Solvent dichloromethane. [f] EtO; 139.7 (570 Hz). [g] MeO; 61.9 (330 Hz). [h] NO$_2$; 576.9 (600 Hz). [i] EtO; 150.8 (80 Hz).

acetonyltriphenylphosphonium ylide **2** (373 ppm), compared with acetamide[17] and methyl acetate,[17] though differences in solvent and in PR$_3$ groups do not allow a closer comparison. Relative to simple ketones (acetophenone $\delta_O = 549$,[17] acetone $\delta_O = 571$[17]), the introduction of the ylide group causes a shift $\Delta\delta_O$ of > -200 (upfield). In the ethoxycarbonyl-substituted triphenylphosphonium ylide **3** the carbonyl group is doubly deactivated by electron donation from the ethoxy and carbanion groups. As a result, δ_O appears at even higher field (271 ppm) than in the keto ylides; this can be compared with other doubly deactivated systems like diethylcarbonate (EtO)$_2$CO, 240 ppm[18] and urethane NH$_2$COOEt, 233.2 ppm (EtO: 121.7 ppm; line widths 120, 130 Hz, respectively, in acetonitrile). Comparing **3** with related acetates, *e.g.* MeCO$_2$Et: 356 ppm,[18] the supplementary deactivation by the ylide group causes an increase of shielding $\Delta\delta_O$ of *ca.* -80 on the ester carbonyl. The difference of $\Delta\delta_O$ values between ketones (-200 ppm) and esters (-80 ppm), agrees, of course, with the expectation that the ester group interacts less than the keto group with the carbanion, and is consistent with the known chemical facts.[2] An evaluation of the substituent effect in **1a–c** is not possible, for scarcity of data, but it appears to be low, not far from those of amides and esters.

To evaluate whether in **1–3** the inductive influence of the positive charge is responsible for the observed increased shielding of the carbonyl oxygen, we have compared, in a non-conjugated system, the δ_O values of three phenacylphosphonium ions **6a–c** with those of other phenacyl compounds (see Table 2). The character of all groups X in PhCOCH$_2$X has almost no effect on δ_O, even in the presence of strong inductive effects as in PhCOCF$_3$; a slight exception is ω-trimethylsilylacetophenone, the only compound of the series with an inductive donor character of X. The estimated arene substituent sensitivities, too, correspond to typical ketones: ArCOCH$_3$ $\rho^+ = 22$,[13] ArCOCH$_2$Br ρ^+ *ca.* 20, ArCOCH$_2$PMe$_3$$^+Br^-$ ρ^+ *ca.* 22.

For diazoacetophenone **4a** we found $\delta_O = 440$, *i.e.* *ca.* 100 ppm downfield from the carbonyl ylide **1a**. The carbonyl O of ethyl diazoacetate **5** appears at $\delta_O = 321$, more shielded than in the diazoketone **4a**, again because of the double deactivation of the carbonyl group, and in agreement with the chemical facts. In order to evaluate the electrophilicity of the carbonyl group in **4a** using the 'tool of increasing electron demand', we have measured the δ_O values of seven *p*-substituted diazoacetophenones **4b–h** (see Table 1) and have evaluated the substituent effect coefficient. We found $\rho^+ = 9.9$ ($r = 0.984$, SD $= 1.03$), a value close to those of amides ($\rho^+ = 7$) and esters ($\rho^+ = 8.5$),[13] confirming the high degree of resonance in diazocarbonyl compounds.† However, the δ_O values of the diazocarbonyl compounds lie considerably downfield from those of amides, esters and carbonyl ylides. They thus deviate from the general δ_O/ρ^+ correlation line (see Fig. 1); the same had been found for carbonyl compounds PhCOX in which the atom directly bound to the carbonyl carbon belongs to a third row element, like Si, P or S[14] (see Fig. 1). For these compounds we shall have to consider downfield shifting influences other than electron density/bond order.

Discussion

Influence of the Electronic Excitation Energy.—On the basis of the theoretical equation (1) of Karplus and Pople[19] the

$$\sigma^P = \mathrm{const.}\Delta E^{-1}\langle r^{-3}\rangle \Sigma Q \qquad (1)$$

paramagnetic shielding σ^P, which makes the main contribution to variations of the shift values of nuclei other than H, depends upon three terms: (a) The bond-order/charge-density term ΣQ, which is related to the π-bond order and thus to the electrophilicity of the carbonyl group; (b) the volume r^3 of the p orbital on oxygen, which is difficult to evaluate and might be included here in (one of) the two other terms; and (c) the electronic excitation energy ΔE, often approximated by the longest-wave UV–VIS absorption. However, only the (electrically) forbidden transitions (*e.g.* $n \longrightarrow \pi^*$) are magnetically active; they give downfield shifts in NMR spectra.[20] It has been shown that the three terms of eqn. (1) are to a certain degree, but not completely, independent from one another.[14]

The phenacylphosphonium ylide PhCOCHPPh$_3$ shows an absorption at $\lambda_{max} = 328$ nm with $\varepsilon = 10\,200$,[8] the acetonyl analogue **2** 295 nm (4400)[8] and the ester **3** 288 nm (3100, in MeCN). On the basis of solvent effects these bands have been attributed to $\pi \longrightarrow \pi^*$ transitions;[2] even in the absence of confirmation by MO calculations, the high extinction coefficients confirm that these transitions are symmetry-allowed, which makes them magnetically inefficient. In this case an influence of

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† *Note added in proof.* Recently, several of the diazoketones listed in Table 1, studied in a different solvent, yielded a ρ^+ value close to that given here. G. Ceriuni, N. Culeddu and A. Saba, *J. Phys. Org. Chem.*, 1992, **5**, 424.

Table 2 ^{17}O NMR chemical shifts of phenacyl compounds

Compound	δ(CO)	*w*[a]	
$PhCOCH_3$	549[b]		
$PhCOCH_2CH_3$	540[b]		
$PhCOCH_2Cl$	542.2	190	
$PhCOCH_2Br$	544.5	240	
p-$MeOC_6H_4COCH_2Br$	528.4	540	MeO; 62.7
p-$NO_2C_6H_4COCH_2Br$	560.5	700	NO_2; 579.3
$PhCOCH_2PMe_3^+Br^-$ (**6a**)	543.8[c]	740	
p-$MeOC_6H_4COCH_2PMe_3^+Br^-$ (**6b**)	530.2[c]	850	MeO; 65.5
p-$NO_2C_6H_4COCH_2PMe_3^+Br^-$ (**6c**)	566.9[c]	*d*	NO_2; 579.7
$PhCOCH_2SiMe_3$	524.4	290	
$PhCOCF_3$	544[e]		

[a] Line width at half height, in Hz (after deduction of 100 Hz line-broadening). [b] See ref. 17. [c] Solvent; MeCN with 8–14% MeOH. [d] Line width modified by the NO_2 signal. [e] See ref. 13.

ΔE would be absent (or at least not bigger than in carbonyl compounds in general) and ΣQ would be the most important factor in determining δ_O of carbonyl ylides. (For a further argument in favour of the absence of a disturbing ΔE influence, see below.)

On the other hand, diazocarbonyl compounds show typical symmetry-forbidden, weak UV absorption at comparably long wavelengths: **4a** has λ_{max} = *ca.* 400 nm (ε = 25),[21] **5** at 389 nm (ε = 14).[22] On the basis of solvent effects these bands have been attributed to $n \longrightarrow \pi^*$ transitions,[21] by MO analysis to (equally symmetry-forbidden) $\pi \longrightarrow \sigma^*$.[23] Thus one has to conclude, following eqn. (1), that the shift values of **4** and **5** contain substantial downfield contributions due to the ΔE term.

Using eqn. (1) one can make a rough estimation of the order of magnitude of the downfield shifting contribution of the ΔE term in **4a**, reducing it to that of the $n \longrightarrow \pi^*$ band in benzamide or methyl benzoate (λ = 275, 276 nm[24], respectively): σ^p, obtained *via* $\delta_O = \sigma^p + \sigma^d$,[20] is multiplied by the ratio of the λ values. Using for the diamagnetic shielding the value of $\sigma^d = -450$ ppm[25,20] (and the absolute scale of shielding and shifts, the zero of which is at 308 ppm of the habitual scale[26]), one obtains a ΔE contribution $\Delta\delta$ = *ca.* 180 (downfield), a value comparable with that estimated from Fig. 1 (*ca.* 120).

Resonance in Carbonyl Ylides.—Schlosser, Jenny and Schaub[3] have recently compared the ^1H and ^{13}C NMR signals of a keto ylide (analogous to **1**) and of the ester ylide **3** with those of suitable reference compounds ($Ph_3P^+CH_2^-$ as model for **B**, $Ph_3P^+CH{=}CH_2$ as model for **C**). They concluded that the true electronic situation of both compounds is about half-way between ylide-like (**B**) and betaine-like (**C**). To evaluate our ^{17}O NMR results in an analogous manner, we chose as reference for **B** the typical keto signal at 540 ppm, for **C** the Li-enolate of propiophenone[27] $PhC(O^-Li^+){=}CHMe$ at 113 ppm. The δ value of **1** (327) then gives *ca.* 50% weight to the keto formula **B**; from the ^1H as well as from the ^{13}C NMR signals one calculates (following ref. 3) equally *ca.* 50%. Applying the same procedure to **3** (271 ppm), with ethyl acetate (356 ppm[18]) as reference for the carbanion formula **B** and the same Li-enolate (113 ppm) for the betaine formula analogue **C**, we find *ca.* 60–70% weight of carbanion in **3**, the same as calculated from ^1H and from ^{13}C NMR spectroscopy.[*] Though the close resemblance of the percentage figures is, of course, fortuitous, one can conclude, as the result from two different systems of comparison, that in the keto phosphonium ylide **1** the weight of the formulae **B** and **C** is *ca.* 1:1, and in the ester ylide **3**, with lower electron attraction, it is *ca.* 2:1.

There are clearly several sources of error in these estimations. However, all corrections of the shift values of the model compounds would be small (*ca.* 20–30 ppm) relative to their overall distance of several hundred ppm. Therefore the possible variations of the results would fall within the limits of uncertainty of our rough estimates. (a) Ketones, too, show a forbidden UV band: PhCOMe 320 nm, ε = 48;[24] however, correcting for the resulting low-field shift, using as reference value $PhCO_2Me$ (λ = 276 nm[24]) would introduce only a slight modification of the estimate. (b) Enolates, too, are resonance hybrids: $-C(O^-){=}CR_2 \longleftrightarrow -C({=}O){-}C^-R_2$. Although the exact position is not known, it is generally admitted that the charge resides predominantly, if not exclusively on O.[28] This is confirmed by the finding that our δ_O value of the enolate is close to that of the enol $PhC(OH){=}CHCO_2Et$ (109 ppm[27]) and of vinyl ethers, *e.g.* $EtOC{=}CH_2$ (88 ppm[29]); thus δ_O of the chosen model cannot be far from that of a 'true' enol. (c) The enolate measured is certainly an aggregate, not the free molecule, but again the proximity of its δ value to those of enols and enol ethers makes the difference insignificant for our estimation. (d) Acetals are not simple ethers. However, in ^{17}O NMR spectroscopy geminal OR groups influence each other rather little ($MeCH_2OEt$, δ_O = 6; $MeCH(OEt)_2$, 48; $MeC(OEt)_3$ 58).[30]

It is significant that in the above-mentioned estimations the results from ^1H NMR spectroscopy coincide with those of ^{13}C and ^{17}O NMR spectroscopy: as the downfield shifting activity of anisotropy terms is small or absent with ^1H NMR signals,[20] the coincidence confirms that there is no major disturbing ΔE term in the ^{17}O signal of the keto ylide either.

Conclusions

The ^{17}O NMR shift values of the carbonyl O in carbonyl-phosphonium ylides are similar to those of amides and esters. In the absence of disturbing electronic excitations, the resonance between the ylide (**B**) and betaine (**C**) formulae gives *ca.* 1:1 weight in the keto ylide **1** and *ca.* 2:1 in the ester ylide **3**. In diazocarbonyl compounds downfield shift effects arise from the electronic excitations. However, the substituent sensitivity value ρ^+, indicative of the electrophilicity of the carbon atom of the carbonyl group, is close to those of amides and esters. It results that the resonance state of both types of C-conjugated carbonyl compounds is similar to that of esters and amides, in agreement with the measurements of rotational barriers.

Experimental

^{17}O NMR spectra were recorded on a Bruker WH-360 spectrometer equipped with a 10 mm probe at 48.8 MHz in the Fourier transform (FT) mode without lock. System control, data acquisition and data management were performed by an Aspect-2000 microcomputer. The instrumental settings were as follows: spectral width 50 000 Hz (1025 ppm); 2 K data points; pulse width 33 μs; acquisition time 20 ms; preacquisition delay 5 μs; 1.4–2.3 M scans; measurements were made with sample spinning (27 Hz). An even number (28–32) of left-shifts (LS) were applied to the FID signal; the latter was zero-filled to 8 K words, and exponentially multiplied with a 100 Hz line-broadening factor (LB) before being subjected to the FT. The chemical shifts, measured in *ca.* 0.4 mol dm^{-3} MeCN solution at 40 °C (unless otherwise indicated), are reported relative to $\delta(H_2O)$ = 0.00; dioxane (δ = 0.0) was used as an external standard; downfield shifts are positive. *J* values are given in Hz. The general reproducibility of chemical shift values is *ca.* + 1 ppm (± 0.2 ppm within the same series).

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[*] The total polarisation of the carbonyl group in **3**, under the influence of two donor groups, is of course higher: using a ketone as the basis of comparison, instead of an ester group, one finds <40% carbonyl character.

New Compounds.—p-*Trifluoromethyldiazoacetophenone* (**4f**) was prepared by the standard procedure,[31] and recrystallized from diethyl ether–pentane (1 : 1), m.p. 60–62 °C (Found: C, 50.35; H, 2.5; N, 13.0. $C_9H_5F_3N_2O$ requires C, 50.45; H, 2.4; N, 13.1%).

p-*Methoxyphenacyltrimethylphosphonium bromide* (**6b**). Trimethylphosphine (1.8 g, 24 mmol) was distilled under N_2 into a frozen solution of *p*-methoxyphenacyl bromide (6.6 g, 29 mmol) in dry benzene (30 cm^3) at −30 °C. After standing overnight at room temperature, the solid was filtered off, washed with benzene and diethyl ether, dried and recrystallized from ethanol–ethyl acetate (2 : 1): yield 75%, m.p. 220–222 °C (Found: C, 47.2; H, 5.9; Br, 26.2. $C_{12}H_{18}BrO_2P$ requires C, 47.2; H, 5.9; Br, 26.2%); δ_H(250 MHz; $CDCl_3$) 2.29 (9 H, d, *J* 14.5), 3.86 (3 H, s), 5.06 (2 H, d, *J* 14), 6.94 (2 H, d, *J* 9), 8.09 (2 H, d, *J* 9); *m*/*z* 225 ($M^+ + 1 - HBr$, 100%).

p-*Nitrophenacyltrimethylphosphonium bromide* (**6c**). Prepared and purified as **6b**, m.p. 259–261 °C (Found: C, 41.2; H, 4.7; N, 4.35; Br, 25.0. $C_{11}H_{15}BrNO_3P$ requires C, 41.3; H, 4.7; N, 4.4; Br, 24.95%); δ_H(250 MHz; $CDCl_3$) 2.27 (9 H, d, *J* 15), 5.06 (s, including C_2H_5OH of crystallization), 8.49 (2 H, d, *J* 9), 8.60 (2 H, d, *J* 9); *m*/*z* 240 ($M^+ + 1 - HBr$).

Compounds **1b** and **1c** were prepared from **6b** and **6c**, respectively, using NaH with $KOBu^t$ in THF, but were not purified; they showed ^1H NMR and MS data as expected.

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