# Photochemical and Thermal Reactions of 1-Carbomethoxy-4-phenyl 2,2,3,3-tetramethyl-5-oxabicyclo[2.1.0]pentane (Ia). Characteristic of the Carbonyl Ylide.

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*Sir:*

The photochemical and thermal interconversion of three membered rings with the corresponding singlet and triplet trimethylenes, or heterotrimethylenes, is of interest from both a synthetic (1) and a theoretical (2) viewpoint. We have recently shown that normally unstable trimethylenes can be characterized if stabilized by incorporation into a cyclic structure and by substitution (3). We report here the extension of this study in the oxabicyclo[2.1.0]pentane series, to the title compound, Ia, wherein the carbomethoxy group can stabilize the negative charge (4).



a) R = $C_6H_5$, R' = $CO_2CH_3$
b) R = R' = $C_6H_5$
c) R = R' = 4-$BrC_6H_4$
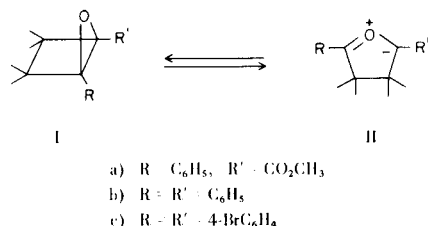
The oxide (Ia) was prepared by *m*-chloroperbenzoic acid oxidation of 1-carbomethoxy-2-phenyl-3,3,4,4-tetramethylcyclobutene (V). When pure, (chromatography on Florisil), Ia is a stable colorless crystalline solid (m.p. 47-48°). Spectral characteristics (ir, uv, nmr) are in accord with the assigned structure; in particular, the nmr spectrum displays five singlets assigned to the nonequivalent methyl groups and a singlet in the aromatic region; nmr (deuteriochloroform) $\delta$ 1.00 (s, 3H), 1.02 (s, 3H), 1.05 (s, 3H), 1.34 (s, 3H), 3.65 (s, 3H), 7.35 (s, 5H).

The required cyclobutene V was obtained by photocycloaddition of methyl phenylpropiolate to tetramethylethylene. If this irradiation were carried out using a high pressure mercury vapor lamp (intense 3660 Å) the major product was the diene VI, formed by photo-valence isomerization of the desired cyclobutene. Reasonable yields of the cyclobutene, free of the diene, could be realized by irradiating with low pressure mercury vapor lamps (predominantly 2537 Å). This wavelength dependence is explicable on the basis of selective excitation of

the acetylene (III) at the shorter wavelength. The absorption maximum of III is 255 nm (cyclohexane, $\epsilon$ = 167,500) while for V $\lambda$ max is 285 (24,400) with a minimum at 230 nm. Indeed, irradiation of V with the high pressure mercury vapor lamp gave VI.
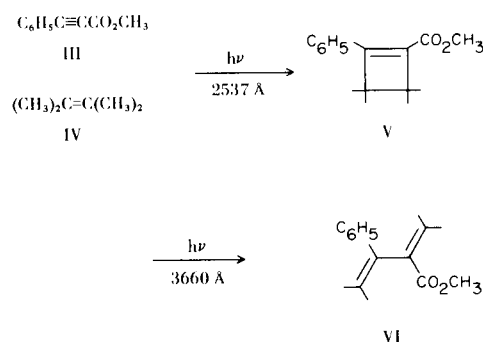


When degassed solutions of Ia were irradiated (2537 Å) at room temperature the colored carbonyl ylide IIa was formed. The long wavelength absorption maximum for IIa is very similar to that for the other derivatives (IIb, c) (3a) as is shown in Table I. These solutions also became colored upon heating above 100°.

TABLE I

Visible Absorption Spectra Assigned to the Carbonyl Ylide II.

| Carbonyl ylide (II) | Solvent | $\lambda$ max (nm) |
|---|---|---|
| a | Benzene | 545 |
| a | Diglyme | 550 |
| b | Diglyme | 544 |
| b | Benzene | 550 |
| b | Decalin | 546 |
| c | Benzene | 558 |

The color disappeared both from the irradiated solutions (first-order process (Table II)) and from the heated solutions upon cooling. The nmr spectrum of dark blue-purple solutions of IIa at 170° showed only starting material. There was no evidence of broadening of the singlets attributed to the methyl groups at this temperature. Solutions kept at 170° for several hours turned colorless upon cooling and the nmr spectrum gave no indication of decomposition; Ia could be recovered.

### TABLE II

First-order Rate of Decomposition of Carbonyl Ylide II.

| Carbonyl Ylide (II) | Solvent | Half-life (min. at 22°) |
|---|---|---|
| a | Benzene | 21 |
| a | Diglyme | 32 |
| b | Benzene | 8 |
| b | Diglyme | 16 |

The carbonyl ylide IIa has a significantly longer lifetime than the diphenyl derivative IIb (3a) indicating that the carbomethoxy group does stabilize the carbonyl ylide to some extent. Even so, the rate of formation of the ylide at 170° is not rapid enough ($k_{exc} < 6 \pi$ sec$^{-1}$) to cause the ring methyl signal in the nmr to broaden, and high temperatures ($\sim 100°$) are required to produce a significant (visible) concentration of the ylide.

When the oxide Ia was heated to 120° in the presence of cyanobenzene, good yields of methyl-2,4-diphenyl-oxazole-5-carboxylate (VIII) were obtained, together with tetramethylethylene. The structure of VIII was rigorously established by comparison (ir, nmr, m.p., mixed m.p.) with an authentic sample (5). The other possible isomeric oxazole was not detected (nmr, tlc) in this reaction mixture. The specificity for formation of VIII (via the
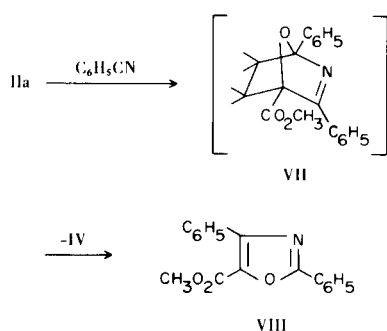


retro Diels-Alder reaction of VII) can be explained on the basis of polar factors wherein the more nucleophilic carbon of the dipole (that bearing the carbomethoxy) bonds to the more positively polarized carbon of the nitrile

moiety.

A degassed benzene solution of Ia, in a quartz esr tube, was irradiated with a low pressure mercury vapor lamp. The highly colored sample, at room temperature, had a small esr signal which became more intense as the color faded and persisted long after the solution had returned to colorless. The proton hyperfine splitting consisted of seven equally spaced lines (all = 1.2 G). There was no evidence of the signal observed previously from the decomposition of IIb (3b). Neither the highly colored sample nor the colorless solution with the strong radical signal had a detectable signal at -196° in the region where a triplet would be expected to absorb.

There are very few classes of free radicals which are as stable as those observed from the decomposition of IIa-c (6). Most radicals derive stability from combinations of extensive delocalization of the free electron, steric factors, and electrostatic repulsion (in charged radicals). The large proton hyperfine splitting observed for the radicals from IIa-c indicate that these radicals are *not* extensively delocalized and suggests that the stability is largely the result of electrostatic repulsion as is the case with ketyl radicals. Experiments designed to test this hypothesis are in progress.

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