- 10. S. Ladas, R. A. Dalla Betta, and M. Boudart, J. Catal., <u>53</u>, 356 (1978).
- 11. S. R. Rafikov, S. A. Pavlova, and I. I. Tverdokhlebova, Methods for the Determination of Molecular Weight and the Polydispersion of High-Molecular-Weight Compounds [in Russian], Izd. Akad. Nauk SSSR, Moscow (1963), pp. 281, 322.
- 12. K. Mackey, Metal Hydrogen Compounds [Russian translation], Mir, Moscow (1968), p. 119.

PHOTOCHEMICAL REACTION OF BENZALDEHYDE AND BENZYL ALCOHOL WITH

METHYL ACRYLATE

I. M. Vol'pin and É. P. Serebryakov

UDC 541.14:542.91:547.571+ 547.568.1:547.391'261

The photochemical addition of alcohols to  $\alpha,\beta$ -unsaturated acids sensitized by benzophenone has been studied by Schenck [1] and Pfau [2-4]. In order to obtain  $\gamma$ -alkyl- $\gamma$ -butanolides, we studied the photolysis of systems containing RCH<sub>2</sub>OH, RCHO, and methyl acrylate (MAC), where R = C<sub>2</sub>H<sub>5</sub>, n-C<sub>5</sub>H<sub>11</sub>, n-C<sub>11</sub>H<sub>23</sub>, and Ph (see the work of Majetti [5]). It has been assumed that a sufficient quantity of RCHOH radicals could be produced in the system such that the addition of these radicals to MAC would compete successfully with the rapid photopolymerization of MAC to (MAC)<sub>n</sub> [6] by selection of suitable concentrations of RCH<sub>2</sub>OH, RCHO (the excited component), and MAC.

The irradiation of aliphatic RCH<sub>2</sub>OH and RCHO with variation of the ratio of these components in Pyrex ( $\gamma > 290$  nm) and in quartz ( $\gamma > 210$  nm) leads almost completely to polymerization and/or telomerization of MAC.

The photolysis of mixtures of PhCH<sub>2</sub>OH and MAC and, in particular, of PhCH<sub>0</sub>, PhCH<sub>2</sub>OH, and MAC leads to 4-phenyl-4-butanolide (I) with yields up to 3.5%. However, the major low-molecular-weight reaction product for all the reagent ratios studied was the methyl ester of 4-meth-oxycarbonyl-6-oxo-6-phenylhexanoic acid (II), which was characterized by its spectral properties. In particular, the strong ion peak with m/z 120 (C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>) in the mass spectrum of (II) corresponds to



the McLafferty fragmentation. The separation of (I) and (II) on  $SiO_2$  and  $Al_2O_3$  is not achieved in many solvent systems due to their similar  $R_f$  values. The separation of pure (I) and (II) by repeated thin-layer chromatography on silica gel is accompanied by loss of the product. However, (I) and (II) are readily separated by gas-liquid chromatography. The yields of (I) and (II) and their ratio in the photolysate are given in Table 1.

A mixture of d, 1- and meso-dihydrobenzoins (III) was isolated in 4-7% yield from the photolysate in addition to (I) and (II). This mixture is formed as the only reaction product in yields from 17% to 40% over 8 h upon the photolysis of mixture of PhCHO and PhCH<sub>2</sub>OH in benzene. The reaction is first-order relative to PhCHO and PhCH<sub>2</sub>OH and the rate constant  $k = (0.89 \pm 0.05) \cdot 10^{-4}$  liter/mole·sec at 20°C.

The initial rates for the consumption of PhCHO upon irradiation with PhCH<sub>2</sub>OH in benzene solution are almost invariant in the presence of MAC, which indicates identical initiation steps.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2384-2387, October, 1985. Original article submitted November 30, 1984.

2209

TABLE 1. The Effect of the PhCHO:PhCH<sub>2</sub>OH:MAC Ratio on the Photolysis Product Yield for  $\lambda > 290$  nm at 20-22°C in Benzene (8 h under argon)

Initial concentration, M			Yield, %*		(II)/(I)
PhCHO	PhCH <sub>2</sub> OH	MAC	· (I)	(II)	chromato- graphic data)
0,10  0,10 0,40	0,40 4,00 0,20 0,40	0,20 0,20 0,20 0,20 0,20	$ \begin{array}{c} 0(0.8) \\ 2(5.5) \\ 3,5(8) \\ 2,5(4) \\ 2(3.5) \end{array} $	$ \begin{array}{c} 2(4,5) \\ 9(21) \\ 10(18) \\ 11(24) \\ 16(28) \end{array} $	5,6 3,8 2,2 6,0 8,0

\*Relative to MAC after separation by thin-layer chromatography. The yield determined by gas-liquid chromatography using an internal standard is given in parentheses.

Reagent concentration, mole/liter	$v_0 \cdot 10^6$ moles/liter $\cdot$ sec
PhCHO $- 0.10$ ; PhCH <sub>2</sub> OH $- 0.20$ ; MAC $- 0.00$ PhCHO $- 0.10$ ; PhCH <sub>2</sub> OH $- 0.20$ ; MAC $- 0.20$	1,77 1,84
PhCHO = 0,10; PhCH <sub>2</sub> OH = 0,20; MAC = 0,20 PhCHO = 0,10; PhCH <sub>2</sub> OH = 0,40; MAC = 0,00	3,46
PhCHO $- 0,10$ ; PhCH <sub>2</sub> OH $- 0,40$ ; MAC $- 0,20$	3,58

Cerfontain et al. [7] and Kawenoki et al. [8] have recently described the photosensitized C-addition of aldehydes to  $\alpha,\beta$ -unsaturated esters in benzene leading to esters of  $\gamma$ -ketocarb-oxylic acids. Kawenoki et al. [8] consider that the reaction is initiated by the formation of a pair of RCO and RCHOH radicals upon the collision of RCHO\* in the T<sub>1</sub> state with RCHO; RCO adds to the double bond, while RCHOH terminates the chain at the stage of the 1:1 adduct. The mechanism for the formation of the 1:2 adduct (II) in PhCH<sub>2</sub>OH probably differs from that proposed by Kawenoki et al. [8] and may be explained by another scheme:

 $P_{h}CH_{2}OH + MAC * \rightarrow PhCHOH + CH_{3}CHCOOMe$ (1)  $P_{h}CHO* + P_{h}CHOH \rightarrow 2P_{h}CHOH$ (1)

$$\operatorname{PROHO}^* + \operatorname{PROH}_2 \operatorname{OH}^* \to 2\operatorname{PROHOH}^* \tag{1'}$$

 $2PhCHOH \rightarrow (III)$ (2)

(6)

 $PhCHOH + MAC \rightarrow PhCH(OH)CH_{2}CHCOOMe$ (3)

	PhCH	20H			
PhCH(OH	(4)				
$PhCH(OH)CH_2CHCOOMe + MAC \rightarrow PhCH(OH)CH_2CHCOOMe$					
		(A)	Ĺ CH₄ĊHCOOM e		
$\mathbf{P}\mathbf{h}$	CH <sub>2</sub> CHCOOMe	Ph	CH <sub>2</sub> CH <sub>2</sub> COOMe		
	· · ·	、 、	/ \		

 $\begin{array}{ccc} C & CH_2 \rightarrow C & CH_2 \\ HO & H & CHCOOMe & HO & CH_2COOMe \\ A) & (B) \end{array}$ 

 $Ph\dot{C}(OH)CH_2CHCOOMe + Ph\dot{C}HOH \rightarrow (II) + PhCH_2OH$ 

(Б) CH<sub>2</sub>CH<sub>2</sub>COOMe

In the absence of PhCHO (see Table 1), the formation of (I) and (II) is most likely initiated by reaction (1), while in the presence of PhCHO, it is initialed by reaction (1'). The rate of reaction (4) which leads in the final analysis to the formation of (I) is less than the rate of reaction (5). The termination of the telomerization of MAC at the stage of radical (A) is the result of a 1,5-hydrogen shift with the formation of the more stable radical (B), which does not tend to abstract a hydrogen atom from  $PhCH_2OH$  but rather is converted to (II) by reaction (7). The yields of (III) decrease with increasing yields of (II).

## EXPERIMENTAL

4-Phenyl-4-butanolide (I) and methyl ester of 4-methoxycarbonyl-6-oxo-6-phenylhexanoic acid (II). A mixture of 5 mmoles PhCHO, 10 mmoles MAC, and 20 mmoles PhCH<sub>2</sub>OH was diluted with benzene to 50 ml and irradiated for 8 h in a flat-bottomed flask with a water jacket. The reactor consisted of Pyrex glass. The DRL-375 lamp was placed in a horizontal pan with a reflecting surface at a distance of 20 cm from the bottom of the flask. The irradiation was carried

out at 20°C under argon. The MAC disappeared entirely as indicated by gas-liquid chromatography. The photolysate was evaporated at 90-100°C (8 mm). The crystals formed were pressed out of the oil and recrystallized from aqueous ethanol to yield 41 mg (4% relative to PhCHO) almost pure meso-dihydrobenzoin (III), mp 130-135°C. The oil was diluted with ether. The solution was filtered to remove the polymer, evaporated, and subjected to chromatography on three silica gel L plates ( $33 \times 22 \times 0.2$  cm) using 5:2 hexane-ethyl acetate as the eluent. The zone with R<sub>f</sub> 0.45-0.55 was resubjected to chromatography on a silica gel L plate ( $33 \times 22 \times 0.2$  cm) using 10:3 chloroform-ethyl acetate as eluent (double pass). The upper zone gave pure (II). The yield was 0.223 g (16% relative to MAC). IR spectrum in CCl<sub>4</sub> ( $\nu$ , cm<sup>-1</sup>): 3040, 1735, 1685, 1600, 1595, 1500, 1270, 1250, 1070, 1010, 690. PMR spectrum in CCl<sub>4</sub> (δ, ppm): 1.95 m (2H), 2.41 t (2H, J = 7 Hz), 3.07 d. t (2H, J = 7 Hz, J' = 1 Hz), 3.48 m (1H), 3.64 s (3H), 3.68 s (3H), 7.43 and 7.90 ( $A_2B_2$ , 4H,  $J_{AB} = 8$  Hz), 7.54 m (1H). Mass spectrum, m/z (relative intensity, %): 278 (0.4), M<sup>+</sup>, 247 (8) [M - 31]<sup>+</sup>, 218 (1.4) [M - 60]<sup>+</sup>, 159 (8), [M - 60 - 59]<sup>+</sup>, 120 (17) [PhCOCH<sub>3</sub>]<sup>+</sup>, 105 (100), 77 (44). The lower zone gave pure (I) in 0.032-g (2%) yield. IR spectrum in CC14 (v, cm<sup>-1</sup>): 3090, 3040, 1770, 1600, 1595, 1500, 1180. PMR spectrum in CC14  $(\delta, \text{ppm}): 1.70-2.55 \text{ m}$  (4H), 5.20 t (1H, J = 6.5 Hz), 7.16-7.29 m (5H). Mass spectrum, m/z (relative intensity, %): 162 (60) M<sup>+</sup>, 117 (44), 107 (65), 77 (62), 56 (100). This product is idnetical to an authentic sample obtained from 4-phenylbutanoic acid according to Nikishin et al. [9].

The kinetic study was carried out by gas-liquid chromatography on an LKhM-8MD chromatograph on a 100  $\times$  0.4 cm column packed with 5% XE-60 on Chromaton N-AW-HMDS with temperature rise at 3 deg/min from 130 to 230°C. The excess nitrogen pressure at the inlet was 1.2 atm. The retention time was 20 min for (I) and 38 min for (II). Similarly, gas-liquid chromatography was carried out on a 150  $\times$  0.4 cm column packed with 0V-225 on Chromosorb P with temperature rise 3 deg/min from 110 to 210°C in order to measure the consumption of PhCHO and Ph-CH<sub>2</sub>OH. A sample of n-C<sub>17</sub>H<sub>36</sub> was used as the internal standard. The v<sub>0</sub> values were determined by the tangent method for [PhCHO]<sub>0</sub>:[PhCH<sub>2</sub>OH]<sub>0</sub> ratios equal to 1:1, 1:2, 1:4, and 2:1 in the absence of MAC and to 1:2 and 1:4 in the presence of MAC. The k value for the photopinacolization was found using a plot of  $\{1/([PhCHO]_0 - x)\}$  vs time and  $\{1/([PhCH<sub>2</sub>OH]_0 - x)\}$  vs time for the other ratios.

## CONCLUSIONS

The major low-molecular-weight product of the photochemical reaction of benzyl alcohol with methyl acrylate, in both the presence and absence of benzaldehyde, is the methyl ester of 4-methoxycarbonyl-6-oxo-6-phenylhexanoic acid (obtained in 2-16% preparative yield). The photolysis of systems containing a primary alcohol, the corresponding aldehyde, and methyl acrylate was found unsuitable for the preparation of 4-substituted  $\gamma$ -butanolides.

## LITERATURE CITED

- 1. G. O. Schenk, G. Koltzenburg, and H. Grossmann, Angew. Chem., 69, 177 (1957).
- 2. R. Dulou, M. Vilkas, and M. Pfau, Compt. Rend. C, 249, 429 (1959).
- 3. M. Pfau, R. Dulou, and M. Vilkas, Compt. Rend. C, 251, 2188 (1960).
- 4. M. Pfau, Compt. Rend. C, 254, 2017 (1962).
- 5. S. Majetti, J. Org. Chem., 37, 2914 (1972).
- 6. L. van der Burg, Rec. Trav. Chim., 41, 21 (1922).
- 7. H. Cerfontain and H. van Noort, Synthesis, No. 6, 490 (1980).
- 8. I. Kawenoki, D. Maurel, and J. Kossanyi, Bull. Soc. Chim. France, Part 2, 385 (1982).
- 9. G. I. Nikishin, É. I. Troyanskii, and I. V. Svitan'ko, Izv. Akad. Nauk SSSR, Ser. Khim., 1436 (1981).