PHOTOCHEMISTRY OF ACETYLENIC COMPOUNDS

9. CYCLOADDITION OF MONOSUBSTITUTED ACETYLENES TO 2-CYCLOPENTEN-1-ONE

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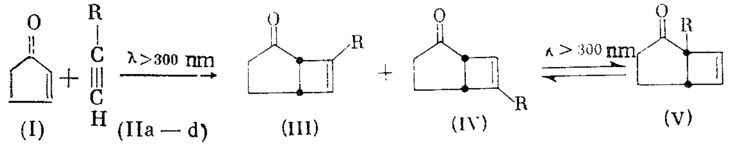
The photocycloaddition of unbranched 1-alkynes to 2-cyclopenten-1-one (I) proceeds with preferential formation of 7-alkylbicyclo[3.2.0]hept-6-en-2-ones [1, 2], i.e., in a "head to head" manner. To elucidate the effect of the nature of the substitutent in monosubstituted acetylenic compounds on the ease and stereospecificity of their addition to α,β-unsaturated cyclic ketones, we have studied the photochemical reaction of (I) with ethoxyacetylene (IIa), propargyl chloride (IIb), propargyl alcohol (IIc), methyl propiolate (IId), and phenylacetylene (IIe).

The cycloadditions were carried out using light with λ > 300 nm in nonpolar solvents at 20-22°. The reaction was followed by GLC and UV spectroscopy. Irradiation was terminated when the rate of disappearance of (I) and of formation of the primary adducts decreased appreciably [at 60-85% conversion of (I)]. After distillation, the product mixture was separated into its individual components by preparative GLC (PGLC), and the ratio of the photolysis products was determined by GLC and PMR. The results are given in Tables 1-3. Reaction of (I) with (IIa)-(IId) results in the formation of comparable amounts of olefinic head-to-head adducts (IIIa)-(IIId) and head-to-tail adducts (IVa)-(IVd), and also a certain amount of the photoisomerization products of the latter, viz., 1-substituted bicylo[3.2.0]hept-6-en-2-ones (Va)-(Vd).



R = OC_2H_5 (a), CH_2Cl (b), CH_2OH (c), $COOCH_3$ (d)

The most complex reaction is that between the cyclopentenone and (IIa): at first, at low conversions of (I), only adducts (IIIa) and (IVa) are formed (in a ratio of ∿1:1.5); this ratio then changes owing to secondary photoconversions of (IIIa) and (IVa). Besides the unsaturated isomer (Va) formed from (IVa) as a result of an acyl 1,3 shift characteristic of 6-alkylbicyclo[3.2.0]hept-6-en-2-ones, the photolysis mixture is found to contain two other isomers, the IR and PMR spectra of which indicate the absence of olefinic bonds. The most intense absorption bands in the IR spectra of both compounds are observed at 1735-1740 (C = O) and 1140-1160 cm^{-1} (—C—O—C—). The first of these cannot be assigned to an ester group because both compounds are readily reduced by $NaBH_4$, and is obviously due to a strained cyclic ketone system. Similar absorption has been observed, in particular, in tricyclo[3.1.1.-0^{6,7}]heptan-2-one formed by the photosensitized isomerization of bicyclo[3.2.0]hept-6-en-2-one [3].

The PMR spectra of both compounds contain signals from the C_2H_5O group and multiplets from seven aliphatic protons at high field. The isomer formed in the smaller amount has a 7H multiplet with a spread of 43 Hz, with the principal signal at δ = 2.36 ppm (Fig. 1a). The isomer formed in the greater amount has a 6H multiplet with a spread of 50 Hz and a one-

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TABLE 1. Reaction of HC ≡ CR (IIa)-(IIe) with Cyclopentenone (I)

R	Reaction conditions*			Reaction products and ratios after photolysis†	Total yield of cycloaddition products, %
	(I):(II) molar ratio	solvent	irradiation time, h.		
OC_2H_5 (a)	1:10	Cyclohexane	40	(Va), (IIIa), (IVa), (VI), (VII) (5:24:27:16:28)	17–23
CH_2Cl (b)	1:5	Ether	42	(VIII), (Vb), (IIIb), (IVb) (14:8:62:16)	26–32
CH_2OH (c)	1:10	Benzene	48	(Vc), (IIIc), (IVc) (11:67:22)	6–9
COOMe (d)	1:3	»	52	(Vd), (IIId), (IVd) (2,5:48,5:49)	6–8
C_6H_5 (e)	1:3	»	60	(XI)	–

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*These are the conditions giving the optimum yields.

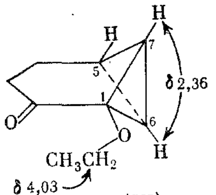
†Listed in order of increasing retention time during GLC; the ratios (in brackets) were determined after distilling off the solvent in vacuo.

TABLE 2. IR Spectra of Bicyclo[3.2.0]hept-6-en-2-ones (III)-(V) [ν, cm^{-1}, in $CHCl_3$ for (IIIc)-(Vc) and CCl_4 for the rest, UR-10 instrument]

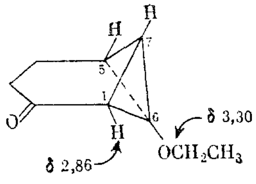
R	(III)	(IV)	(V)
OC_2H_5 (a)	3080, 1745, 1620, 1410 1280, 1190, 1160, 1060		3120, 3055, 1745, 1630, 1450, 1395, 1260, 1210, 1140
CH_2Cl (b)	3068, 1740, 1642, 1455, 1432, 1410, 1300, 1160, 950	3060, 1735, 1620, 1460, 1415, 1265, 1060, 950	3090, 1743, 1680, 1460, 1410, 1260, 1155, 915
CH_2OH (c)	3610, 3480, 3315, 3020, 1729, 1608, 1465, 1410, 1252, 1170, 1060	3620, 3450, 1730, 1605, 1465, 1410, 1260, 1170, 1040	3690, 3620, 3530–3300, 3130, 3020, 1730, 1608, 1460, 1412, 1330, 1080, 1035
$COOCH_3$ (d)	3065, 3025, 1745>1720, 1610, 1435, 1410, 1310, 1282, 1250, 1224, 1135, 1085	3095, 3025, 1745<1720, 1605, 1455, 1435, 1410, 1335, 1308, 1245, 1210, 1140, 1090	

proton multiplet at 2.86 ppm (Fig. 1b). A comparison of the spectra of the two isomers suggests that the minor isomer has the more symmetric structure, with the result that its spectrum is simplified. In addition, the signals from the C_2H_5O protons in the spectrum of the minor isomer appear at lower field ($\delta = 4.03$ and 1.20) than those in the spectrum of the major isomer ($\delta = 3.30$ and 1.08). Evidently, the C_2H_5O group in the former isomer is located beside the carbonyl group and its motion deviates only slightly from the $>C{=}O$ plane, so that it is deshielded. Since the photoisomerization of bicyclo[3.2.0]hept-6-en-2-ones to tricyclo-$[3.1.1.0^{6,7}]$heptan-2-ones is known [3], the most probable structures fitting the indicated spectral data are (VI) for the minor isomer and (VII) for the major isomer. In particular, the principal signal in the 7H multiplet in the PMR spectrum of the minor isomer appears in the range characteristic of the protons of the bicyclobutane fragment [3], and the broadening of the one-proton multiplet at $\delta = 2.86$ ppm in the spectrum of the major isomer is in accord with the presence of a strong interaction between H^1 and H^5 through four σ bonds arranged in an M shape; this kind of interaction is characteristic of related bridging systems containing a four-membered ring [4, 5] (see scheme on following page).

A study of the dynamics of the conversions of adducts (IIIa) and (IVa) also indicates in favor of structures (VI) and (VII). The (IIIa):(IVa) ratio changes from $\sim$2:3 at the start of photolysis to $\sim$8:9 at the end due to the fact that the reactions (IVa) $\rightleftarrows$ (Va) and (VIa) $\rightarrow$ (VII) go more rapidly than the isomerization (IIIa) $\rightarrow$ (VI). When the pure (Va) isomer in cyclohexane is irradiated with light of wavelength $\lambda > 300$ nm, the reactions (Va) $\rightleftarrows$ (IVa) and



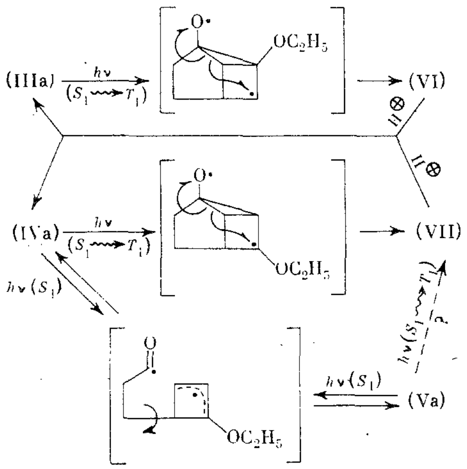
(VI)



(VII)

(Va) → (VII) are also observed to proceed in parallel, the latter going approximately twice as fast as the former, while isomer (VI) is not formed. The latter is evidently the product of an acyl 1,2 shift (oxa-di-π-methane rearrangement) in enone (IIIa). When irradiated, the separate (VI) and (VII) isomers are not converted into (IIIa) or (IVa), and one is not converted into the other; instead, they gradually decompose to form several unidentified carbonyl compounds. In the presence of traces of acid, (VI) and (VII) rapidly isomerize to (IIIa)-(IVa) (IR and GLC data).

Oxa-di-π-methane photorearrangement of β,γ-unsaturated ketones generally proceeds in the presence of triplet sensitizers [6], and cases of unsensitized acyl 1,2 shifts are rare [7-10]. The formation of compounds (VI) and (VII) observed in the course of the reaction of (I) with (IIa) is yet another exaple of this kind of unsensitized rearrangement.* In this case, the rearrangement of the vinyl ether in enones (IIIa) and (IVa) evidently causes deactivation of their singlet states, with the result that the rate of the acyl 1,3 shift proceeding by a singlet mechanism [12] and leading to (IVa) ⇄ (Va) interconversion becomes comparable with the rate of intersystem crossing ($S_1 \quad T_1$) necessary for rearrangement to (VI) and (VII). It is known that vinyl ethers effectively quench the singlet states of ketones by forming charge-transfer complexes [13, 14].



The reaction of (I) with chloride (IIb) in ether proceeds less ambiguously. Only adducts (IIIb) and (IVb) are formed (in a ratio of ∿3:1) at the start of photolysis, after which isomer (Vb) appears. Towards the end of photolysis a product of the addition of the solvent to (I) is also formed. This was identified on the basis of a combination of IR, PMR, and mass-spectral data as being the known [15] compound 3-(1-ethoxyethyl)cyclopentan-1-one (VIII). Photolysis of the individual isomers (IVb) and (Vb) leads to rapid equilibrium interconversion until a (IVb):(Vb) ratio of 1.8 is obtained.

The reaction of (I) with alcohol (IIc) in benzene proceeds slowly, and the primary adducts (IIIc) and (IVc) tend to undergo photopolymerization and form minor secondary products of indeterminate structure. The (IIIc):(IVc) ratio is initially ∿4 in benzene and ∿2.5 in ether, decreasing to 2.3 and 0.45 respectively towards the end of photolysis; isomer (Vc) is also observed in the photolysis mixture. Photolysis of the individual isomers (IVc) and (Vc) leads partly to their conversion into an equilibrium mixture [(IVc):(Vc) ≈ 2] and partly

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*The cyclopentenone (E_T = 60-61 kcal) cannot act as a triplet sensitizer for β,γ-enones (E_T = 68-73 kcal, see [11]), and the principal rate of formation of (VI) and (VII) by direct photolysis of (IIIa)-(IVa) and (Va) is greater than their rate of accumulation under cycloaddition reaction conditions.

TABLE 3. PMR Spectra of Bicyclo[3.2.0]hept-6-en-2-ones (III)-(V)* (δ, ppm, Varian DA 60 IL, J, Hz)

R	(III)	(IV)	(V)
OC_2H_5† (a)	1,20 t (3H, J=6,5); 1,70–2,80m (4H); 3,05 m (1H); 3,20 m (1H); 3,70 q (2H, J=6,5); 4,60 br.s (1H)	1,25 t (3H, J=6,5); 1,70–2,80m (4H); 3,05m (1H); 3,33m (1H); 3,80 q (2H, J=6,5); 4,50 br.s (1H)	1,13 t (3H, J=6,5); 1,55–2,75m (4H); 3,26 m (1H); 3,50 q (2H, J=6,5); 6,17 and 6,35 (AB system 2H, J_{AB}=2,9)
CH_2Cl (b)	1,70–2,85 m (4H); 3,05 m (1H); 3,25m (1H); 3,80 m (2H); 6,23 s (1H)	1,70–2,80 m (4H); 2,90 m (1H); 3,39 m (1H); 3,95 s (2H); 6,00 s (1H)	1,65–2,80 m (4H); 2,20m (1H); 3,69 s (2H); 5,89 5,92 (AB, 2H, J_{AB}=3)
CH_2OH (c)	1,75–2.60 m (4H); 3.00 m (1H); 3,21 m (1H); 3,83 br.s (2H); 6,08 s (1H)	1,75–2.60m (4H); 3,00m (1H); 3,31 m (1H); 4,00 br.s (2H); 5,81 br.s (1H)	1,80–2,75 m (4H); 3,23 m (1H); 3,65 and 3,75 s and br.s (2H); 6,05 and 6,31 (AB, 2H, J_{AB}=2,8)
$COOCH_3$ (d)	1.90–3,00m (4H); 3,30–3,43 m (2H); 3,70 s (3H); 7,13 s (1H)	1,80–2,60 m (4H); 3,00 m (1H); 3,22 m (1H); 3,76 s (3H); 6,79 s (1H)	5,93 and 6,06 (AB, 2H, J_{AB}=2,8)

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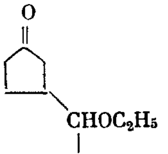
*In $CDCl_3$ for (IIIc), (IIId), (IVc), (IVd), and (Vc); in CCl_4 for the rest. The spectra of (IIIc)-(Vc) in CD_3OD are of the same form as in $CDCl_3$.

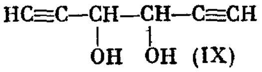
†The assignments in the spectra of the mixture of (IIIa) and (IVa) were correlated with GLC data for this mixture.

to their polymerization. When isomer (IIIc) is photolyzed, it polymerizes and is converted into unidentified secondary products, but not into (Vc). The reaction mixture was found to contain a small amount of a glycol (IX), which was identified as 1,5-hexadiyne-3,4-diol [16].

The reaction of (I) with methyl propiolate (IId) in benzene also proceeds slowly and gives practically only two products, viz., isomers (IIId) and (IVd) in a ratio of ∿1:1. Under the influence of light with λ > 300 nm, isomer (IIId) polymerizes only slowly, and the photopolymerization of (IVd) proceeds very slowly. The presence of isomer (Vd) in the photolysis mixture was established by its PMR spectrum, which shows a very weak signal due to the AB system formed by the two olefinic protons of the cyclobutene ring (δ = 5.93 and 6.06, J_{AB} = 2.8 Hz)

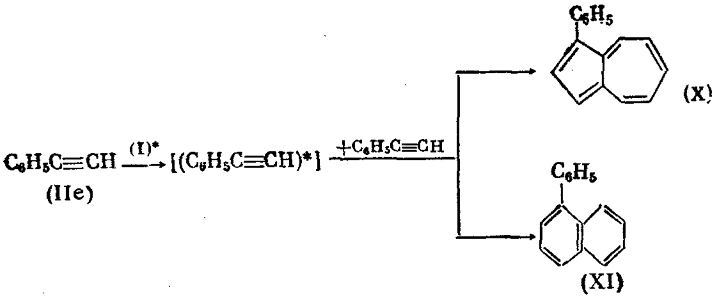


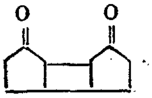
(VIII)



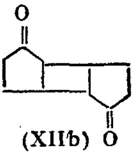
$$HC{\equiv}C{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}{-}C{\equiv}CH$$

(IX)





(XIIa)



(XIIb)

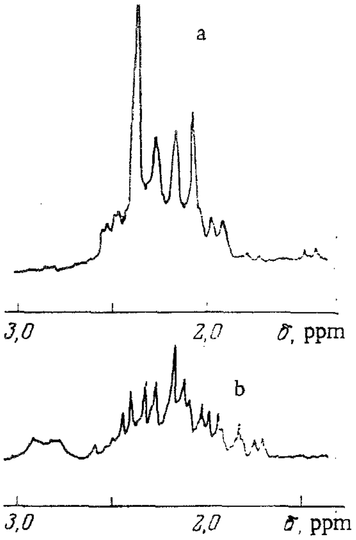


Fig. 1. The PMR spectra of tricyclo[3.1.1.$0^{6,7}$]heptan-2-ones at high field: a) 1-ethoxy isomer (VI); b) 6-ethoxy isomer (VII).

Finally, reaction of (I) with phenylacetylene (IIe) in benzene gives no cycloadducts of type (III) and (IV). Instead, small amounts of 1-phenylazulene (X) and 1-phenylnaphthalene (XI) are formed, and the rate of disappearance of (I) is very low. Since (IIe) does not absorb light with $\lambda > 300$ nm, the energy necessary for the dimerization of (IIc) to hydrocarbons (X) and (XI) is probably transferred from the excited state of (I) to the ground state of (IIe). A similar example of photosensitized dimerization has recently been observed in [17].

The reactions of (I) with (IIa), (IIb), (IIc), and (IId) are also accompanied by the formation of crystalline cyclopentenone dimers (XIIa) and (XIIb), the yields of which (3-10%) increase as cycloaddition becomes more difficult.

Structures of type (III), (IV), and (V) can be distinguished by their spectral properties In the PMR spectra of isomers of type (III) the signal from the olefinic proton appears at weaker field than in the spectra of isomers of type (IV), and in the spectra of isomers of type (V) the olefinic protons form an AB system with $J_{AB} \sim 2\text{-}3$ Hz (see Table 3). In the IR spectra of adducts (IIId) and (IVd) the intensity ratio of the carbonyl absorption bands of $>C{=}O$ and $COOCH_3$ are different, and the IR spectra of (Vc) shows an intramolecular H bond (see Table 2).

The mass spectra of adducts of type (III) show a high-intensity $C_5H_6O^+$ ion with $m/e = 83$, whereas the spectra of the type (IV) and (V) compounds are characterized by more chaotic fragmentation.

EXPERIMENTAL

The reactions of (I) with (II) were carried out at 18-20° in a cylindrical reactor (capacity 300 ml) equipped with a bubbler, a reflux condenser, and a DRT-375 lamp with a Pyrex glass water jacket, the lamp being arranged vertically to the axis of the reactor. In each preparative experiment, a 3-10-fold molar excess of (II) was used per 3.0 g (0.036 mole) of (I) (see Table 1), and the reaction volume was adjusted to 250 ml with solvent purified as described in [18].

The photoisomerization of the individual isomers of type (III), (IV), and (V) was carried out at 28-30° (air cooling) in flat-bottomed Pyrex glass flasks (capacity 25 ml) equipped with a bubbler and a refleux condenser and fixed at a height of 25 cm above two PRK-4 lamps (2 × 220 W) arranged horizontally in a reflector tray. The concentration of the solutions of (III)-(IV) was 50 mg in 10 ml of cyclohexane for (Va) $\rightleftarrows$ (IVa) $\rightarrow$ (VII), ether for (IIIb)-(IVb) and (IIIc)-(Vc), or benzene for (IIIc)-(Vc) and (IIId)-(IVd). All experiments were conducted in a stream of dry argon, bubbling of which was started 30 min before irradiation.

Analysis was performed by GLC in an all-glass column (2 m × 3.5 mm) containing 5% PEG 400 on Chromosorb G + 5% KOH (130-175°) and in an all-glass capillary (50 m × 0.7 mm) containing silicone XE-60 at the same temperatures. The PGLC was performed using an LKhS-3 instrument with an all-glass system (2 m × 13 mm; 13% PEG 4000 on Chromosorb A; 110-135°; nitrogen flow rate 200 ml/min). The adduct yields indicated in Table 1 are given relative to the total weight of distillable photolysis products.

The isomer ratios are given as the average of 4-5 chromatograms of the photolysis mixture after evaporating off the solvent in vacuo at 25-30°; the disagreements with the chromatograms of the total distillate were insignificant. Besides using GLC, we also determined the isomer ratios in the distillate by means of PMR spectra; the two methods gave satisfactory agreement. Adducts (IIIa)-(IIId), (IVa)-(IVd), (Va)-(Vc), and (VI)-(VIII) are colorless fragrant liquids.

Ethoxyacetylene (IIa). The total distillate (1.40 g), with a bp of 52-92°/3.5 mm λ (nm, heptane) = 215 (4300), 226 (900 sh), 315 (220), and 326 (105 sh),was separated by PGLC (110°) into the following products: 1) 1-ethoxybicyclo[3.2.0]hept-6-en-2-one (Va), yield 85 mg; 2) a mixture of 7-ethoxy- and 6-ethoxybicyclo[3.2.0]hept-6-en-2-ones (IIIa) and (IVa) in a ratio 45:55, yield 210 mg; 3) 1-ethoxytricyclo[3.1.1.$0^{6,7}$]heptan-2-one (VI), yield 75 mg. M^+ 152, IR spectrum (ν, cm^{-1}, CCl_4) 1740, 1560, 1410, 1380, 1190, 1160, 1040, PMR spectrum (δ, ppm, CCl_4) 1.20 t (3H, J = 7 Hz), 1.80-2.56 m (7H), 4.03 q (2H, J = 7 Hz); 4) 6-ethoxytricyclo[3.1.1.$0^{6,7}$] heptan-2-one (VII), yield 165 mg, M^+ 152, IR spectrum (ν, cm^{-1} CCl_4), 1740, 1450, 1395, 1140, 1060, PMR spectrum (δ, ppm, CCl_4) 1.08 t (3H, J = 7 Hz), 1.70-2.73 m (6H), 2.86 m (1H), 3.30 q (2H, J = 7 Hz). On shaking with dilute HCl in aqueous methanol for 2 h, compounds (VI) and (VII) form products with identical IR and GLC data to the mixture of (IIIa) and (IVa). Reduction of (VI) and (VII) with excess $NaBH_4$ in methanol gives a colorless oil with ν = 3600-3000 cm^{-1}.

Propargyl Chloride (IIb). The total distillate (1.84 g), with a bp of 65-110°/2 mm, was redistilled to give two fractions: 1) bp 41-75°/2 mm 0.17 g; 2) bp 75-108°/2 mm, 1.23 g. From fraction 1) by PGLC we isolated 80 mg of 3-(1'-ethoxyethyl)cyclopentan-1-one (VIII), M^+ 156, m/2 73.43 (main peak); IR spectrum (ν, cm^{-1}, CCl_4) 1745, 1380, 1170, 1130, 1110, 1090; PMR spectrum (δ, ppm, CCl_4) 1.03 and 1.07 comprising superposition of t 3H + d 3H (6H, J = 7 Hz), 1.98 m (7H), 3.30 3.42 comprising superposition of q 2H + m 1H (3H, J = 7 Hz). The PMR assignments were verified by double resonance with added $Eu(DPM)_3$. Fraction 2) was subjected to PGLC (115°) to isolate 70 mg of 1-chloromethylbicyclo[3.2.0]hept-6-en-2-one (Vb), 360 mg of 7-chloromethylbicyclo[3.2.0]hept-6-en-2-one (IIIb), and 130 mg of 6-chloromethylbicyclo[3.2.0]hept-6-en-2-one (IVb).

Propargyl Alcohol (IIc). The total distillate (0.42 g), with a bp of 125-149°/3.5 mm, was separated by PGLC (130°) to give 60 mg of 1-hydroxymethylbicyclo[3.2.0]hept-6-en-2-one (Vc), 126 mg of 7-hydroxymethylbicyclo[3.2.0]hept-6-en-2-one (IIIc), and 82 mg of 6-hydroxymethylbicyclo[3.2.0]hept-6-en-2-one (IVc). The latter was contaminated by a small amount of dimers (XIIa) and (XIIb), which were removed by chromatography on Al_2O_3 plates (with benzene—$CHCl_3$, 3:2, lower zone). The distillation residue of the photolysis products was chromatographed on 20 g of Al_2O_3, eluting with benzene—$CHCl_3$ (2:3), to give 25 mg of liquid diol (IX) with m/e = 57 and 56 (ν, cm^{-1}, $CHCl_3$: 3370, 3310, 2130, 1040). This gave a positive reaction with ammoniacal Ag_2O and formed a diacetate in the form of an oil with m/e = 97 and 99 (ν, cm^{-1}, $CHCl_3$: 3315, 2140, 1750, 1250).

Methyl Propiolate (IId). A portion (0.16 g) of the total distillate (0.64 g), with a bp of 56-71°/3.5 mm and λ_{max} (in heptane) = 212 (4950), 241(2620), 300 (130), 309 (130), 320 (115), and 332 (65) nm, was subjected to preparative TLC on silica gel L plates (240 × 200 × 1 mm, benzene—ether—CH_3CN, 5:2:1). The upper zone comprised 6-methoxycarbonylbicyclo[3.2.0]hept-6-en-2-one (IVd), yield 68 mg. The lower zone comprised 7-methoxycarbonylbicyclo[3.2.0]hept-6-en-one (IIId), yield 82 mg.

Phenylacetylene (IIe). After distilling off the excess (IIe) and unreacted (I) in vacuo, the residue (0.4 g of a green oil) was chromatographed on 20 g of Al_2O_3 with heptane—benzene (9:1). First eluted was 137 mg of 1-phenylazulene [M^+ 204; λ, nm, heptane: 233 (34,600), 296 (36,000), 355 (7600), 373 (7400), 615 (32), 670 (23)], followed by 31 mg of 1-phenylnaphthalene [M^+ 204; λ, nm, heptane: 231 (56,000) and 292 (10,200)].

CONCLUSIONS

1. The photocycloaddition of 2-cyclopenten-1-one (I) to ethoxyacetylene, propargyl chloride, propargyl alcohol, and methyl propiolate results in the formation of comparable

amounts of head-to-head and head-to-tail cycloadducts. Instead of cycloaddition of (I) to phenylacetylene, the latter only undergoes sensitized dimerization to 1-phenylazulene and 1-phenylnaphthalene.

2. The 7- and 6-ethoxybicyclo[3.2.0]hept-6-en-2-ones are observed to undergo unsensitized oxa-di-π-methane rearrangement to 1- and 6-ethoxytricyclo[3.1.1.$0^{6,7}$]heptan-2-ones (VI) and (VII), respectively.

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PHOTOCHEMISTRY OF ACETYLENIC COMPOUNDS

10. EFFECT OF TEMPERATURE AND SUBSTITUENTS ON THE ADDITION OF 2-CYCLOPENTEN-1-ONE TO MONOSUBSTITUTED ACETYLENES

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It is known [1, 2], that the addition of cyclopentenone (I) to linear 1-alkynes proceeds with preferential formation of head-to-head adducts. In the case of the reaction with 1-heptyne (IIa) it has been established that cycloaddition involves the T_1 state of (I); the reaction rate decreases and the relative yield of the head-to-tail adduct increases somewhat on passing from nonpolar to polar solvents [3]. In the case of the cycloaddition of (I) to acetylenes (IIb)-(IIe), the head-to-head adducts (IIIb)-(IIIe) and head-to-tail adducts (IVb)-(IVe) are also formed in comparable amounts [4] (see scheme on following page).

In the present work we have studied the effect of temperature, and also the size and nature of the substituent in (II), on the rate and stereochemistry of the cycloaddition of

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