Photocycloaddition of Dimethyl Acetylenedicarboxylate and Methyl Propiolate to Benzo[b]furans

Alois H. A. Tinnemans and Douglas C. Neckers*[1]

Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403

Received December 21, 1976

The sensitized photochemical [$_\pi 2_s + _\pi 2_s$] cycloaddition of dimethyl acetylenedicarboxylate to benzo[b]furan (Ia) leads to four cyclobutene derivatives in which carboxymethyl groups occupy vicinal positions. We suggest that 1,7-dicarboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (IIIa) arises via the initially formed 6,7-dicarboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (IIa) or from the 5,6-dicarboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (IVa). Compound IVa is shown to be formed both from IIa and from IIIa via a postulated 1,2-cyclobutenospiro[2.5]octadiene as intermediate. Compound IVa could rearrange to 1,5-dicarboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (Va). Sensitized addition of methyl propiolate to Ia produces both the adduct with the carboxymethyl group attached to the 2 position of the benzo[b]furan nucleus and the unrearranged 1:1 adduct, suggesting that the excited state of benzo[b]furan is highly polarized. The cyclobutenes IIIa and IVa rearrange to the corresponding 1-benzoxepins by heating at 180–210 °C. The photocycloaddition of dimethyl acetylenedicarboxylate to 2-methylbenzo[b]furan is more complicated but shows the cycloaddition to be general.

Thermal additions of acetylenic esters to fused heteroaromatic compounds have been extensively investigated[2] and appear to be of great value in the synthesis of fused heterocyclic seven-membered ring systems, e.g., benzo[b]azepine, benzo[b]oxepin, and benzo[b]thiepin. Cyclobutene intermediates could be isolated[3–5] in some cases.

A similar reaction has been reported for the photocycloaddition of acetylenes to benzo[b]thiophene.[6,7] The only alkyne from which an unrearranged 1:1 adduct to benzo[b]thiophene could be isolated was diphenylacetylene while only rearranged cyclobutenes were found when dimethyl acetylenedicarboxylate, methyl propiolate, and methyl phenylpropiolate were used.

We have now investigated the photochemical addition of dimethyl acetylenedicarboxylate and methyl propiolate to benzo[b]furan. It will be shown that the normal rearrangement of the first formed 1:1 photoadduct is followed by a more complex type of photorearrangement.

Results

Irradiation, at $\lambda > 300$ nm, of a mixture of benzo[b]furan (Ia) and dimethyl acetylenedicarboxylate dissolved in deaerated benzene, for 70 h in the presence of the sensitizer, acetophenone, gave a complex reaction mixture. By column chromatography on Florisil, four products could be isolated (IIa–Va) in 9, 8, 7, and 1.5% yield, respectively (Table I). A similar irradiation in benzene without added acetophenone did not lead to substantial photoconversion. However, on irradiation of Ia (E_T = 70 kcal/mol[8a]) in the presence of benzophenone as sensitizer only oxetanes were obtained.[8]

In view of the known direct and photosensitized additions of acetylene derivatives to benzo[b]thiophene,[6,7] it could be supposed that IIa and IIIa also are cyclobutenes. The NMR spectrum of IIIa (Table II) revealed a broad singlet at δ 4.50 ppm, whereas that of product IIa exhibited an AB pattern (J_{AB} = 6.0 Hz) at δ 4.52 and 5.63 ppm. The former values are in good agreement with the chemical shift values of H_5 in 2-thiabenzo[b]bicyclo[3.2.0]hepta-3,6-dienes,[7] while the latter value corresponds to the chemical shift of H_1 in the corresponding 5-pyrrolidino derivative.[4] The mass spectra of these adducts include, as is expected,[7,10] ions from retro-cleavage in a direction such that the benzo[b]furan nucleus remains as the major peak, *m/e* 118 and 176, respectively. Further, the IR spectrum contained an absorption at about 1635 cm^{-1}, within the region expected for the olefinic double bond in annelated cyclobutenes.[4,5,7,11a]

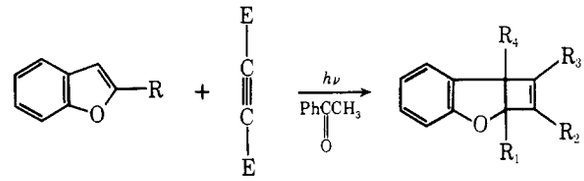
The base peak in the mass spectrum of IVa, *m/e* 176, loss of HC≡CCOOCH$_3$ fragment, pointed out that IVa also should be a cyclobutene adduct. The NMR spectrum showed two singlets at δ 5.51 and 6.78 ppm, fitting in with H_1 and H_7, respectively. It is not surprising that H_1 and H_7 are very weakly coupled ($J \ll 1$ Hz), an observation characteristic of vinyl and allylic protons in cyclobutenes.[7] The UV and IR data of IVa were quite similar to those found for IIIa.

Finally, in analogy to the photoproduct IIIa, product Va is expected to be 1,5-dicarboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene. The NMR spectrum (Table II) was clearly consistent with structure Va.

Compound IVa was isolated as a major product and was shown to derive from either IIa or IIIa by rearrangement (Table III). As a matter of fact, all isomers IIa–Va derived from each of the other isomers when irradiated in the presence of acetophenone as sensitizer.

To gain more insight into the mechanism of this rearrangement the sensitized addition of dimethyl acetylenedi-

Table I. Products of Photocycloaddition of Dimethyl Acetylenedicarboxylate to Benzo[b]furans

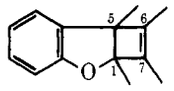


Ia,b, R = H, CH$_3$ E = COOCH$_3$

	Compd	R_1	R_2	R_3	R_4	Yield, %
R = H[a]	IIa	H	E	E	H	9
	IIIa	E	E	H	H	8
	IVa	H	H	E	E	7
	Va	E	H	H	E	1.5
R = CH$_3$[b]	IIb	CH$_3$	E	E	H	5
	IIIb	E	E	CH$_3$	H	15
	IVb	H	CH$_3$	E	E	6
	Vb	E	CH$_3$	H	E	*c*
	IIc	H	E	E	CH$_3$	1
	IIIc	E	E	H	CH$_3$	*c*
	IVc	CH$_3$	H	E	E	2
	Vc	E	H	CH$_3$	E	*c*

[a] Compounds IIa, IIIa, IVa, and Va equilibrate under the conditions of the experiment. The relative yields, therefore, depend on the irradiation time. [b] A photoequilibrium exists among isomers IIb–Vc. The relative yields may therefore vary. [c] These isomers are likely in reaction mixture but were not definitively identified.

Table II. NMR Spectra of Substituted Cyclobutene Systems, Measured in $CDCl_3$ (δ, ppm)



Registry no.	Compd	H_5	H_6	H_7	H_1	$COOCH_3$	$COOCH_3$	CH_3
62250-75-3	IIa	4.52			5.63	3.82	3.84	
62250-76-4	IIIa	4.50	<6.80			3.78	3.88	
62250-77-5	IVa			6.78	5.51	3.79	3.82	
62250-78-6	Va		6.28	6.93		3.82	3.84	
62279-99-6	IIb	4.16				3.84	3.84	1.82
62250-79-7	IIIb	4.35				3.75	3.85	2.19
62250-80-0	IVb				5.40	3.80	3.83	2.09
62250-81-1	IIc				5.28			2.05
62250-82-2	IVc			6.56		3.79	3.89	1.81
62250-83-3	VI	4.62		6.71	5.50		3.82	
62250-84-4	VII	4.57	6.23	6.82			3.88	

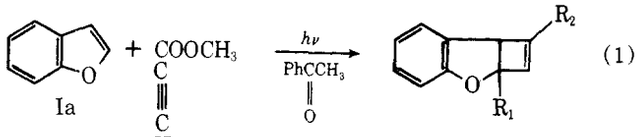
Table III. Rearrangement of Dicarboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-dienes[a]

$h\nu$, h	Starting material	Products[b] IIa	IIIa	IVa	Va
20	IIa	6	50	44	>0
84	IIIa	>0	75	19	6
63	IVa	>0	36	52	12

[a] Irradiated in a solution of benzene (70–115 mg/8 mL), under nitrogen, with acetophenone (20 mol %). [b] Relative yields (%), obtained by NMR analysis (±5%).

carboxylate was also carried out under the same conditions with 2-methylbenzo[b]furan. Of the eight possible isomers (vide infra) at least seven cyclobutene derivatives could be shown in the vapor phase chromatogram of the crude reaction mixture. Five of them could be characterized by NMR spectroscopy (Tables I and II).

Sensitized addition of methyl propiolate to benzo[b]furan (Ia) proceeds similarly to that reported for benzo[b]thiophene[7] (eq 1). Only two photoproducts could be isolated, VI and VII,



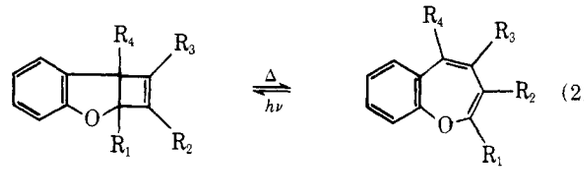
Ia

VI, R_1 = H; R_2 = $COOCH_3$
VII, R_2 = H; R_1 = $COOCH_3$ (1)

in 2 and 4% yield, respectively. The IR spectra again showed an olefinic double bond in an annelated cyclobutene, while the UV spectra were similar to those of IIIa and IVa. The NMR spectrum of VI showed an AB quartet between the allylic protons at δ 4.62 and 5.50 ppm, weakly coupled with the vinylic proton at δ 6.71 ppm, whereas that of VII revealed a broad singlet at δ 4.57 ppm and an AB quartet between the vinylic protons. Irradiation of pure VI in the presence of acetophenone yields the isomer VII as the only new-formed product. Moreover, the alternate 7-carboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene could be dismissed because of the less likely opposite mode of cycloaddition. Nevertheless, a vapor phase chromatogram of the crude reaction mixture shows the presence of this isomer in only a few percent.

The cyclobutene adduct prepared from dimethyl acetylenedicarboxylate and 3-pyrrolidinobenzo[b]furan is thermally only moderately stable and can be converted in refluxing dioxane to give the corresponding benzo[b]oxepine. Prolonged heating in p-xylene (138 °C) gave the isomeric 7-naphthol.[4]

A chemical proof for the structures of the products IIIa and IVa was obtained by thermolysis of the pure compounds at 185 and 210 °C, respectively. This resulted in the 1-benzo[b]-oxepins VIII and IX (eq 2). The NMR spectra[12] for both



IIIa, R_3 = R_4 = H
IVa, R_1 = R_2 = H

VIII, R_1 = R_2 = $COOCH_3$
IX, R_3 = R_4 = $COOCH_3$ (2)

compounds contained an AB pattern at δ 6.08 and 6.51 ppm (J_{AB} = 6.0 Hz) and at 6.39 and 7.06 ppm (J_{AB} = 11.5 Hz), respectively. The UV absorptions of both VIII and IX showed a long-tailed absorption into the visible region, caused by the oxepin chromophore.[12b-d]

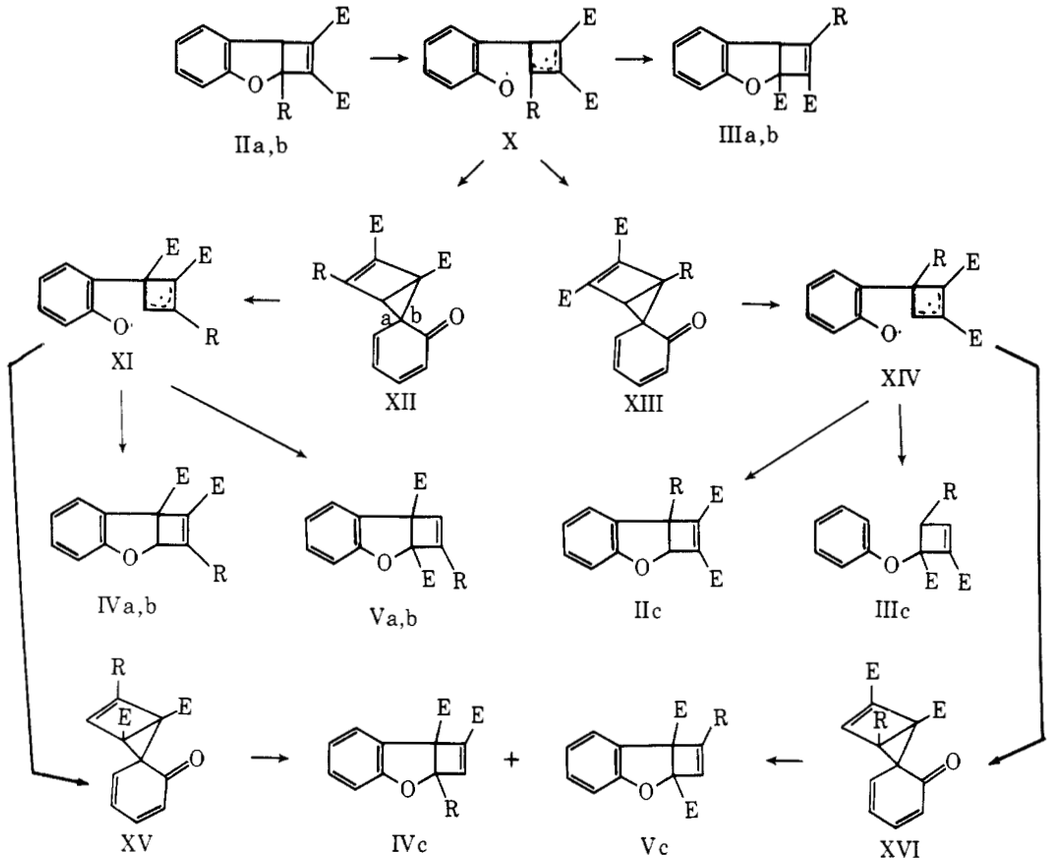
As expected, upon irradiation at $\lambda > 300$ nm, the 1-benzo[b]oxepins VIII and IX are reconverted into the corresponding cyclobutenes IIIa and IVa, respectively (eq 2). This reaction, an electrocyclic ring closure of the diene system, has been observed for other heterocyclic compounds as well.[13] It results from a symmetry-allowed disrotatory reaction which leads to cis annelation of the two rings.

Discussion

The UV spectrum of benzo[b]furan[14] possesses a sharp absorption maxima in the 266–281-nm region, with a maximum absorption at 281 nm (ϵ 3300). Above 286 nm (ϵ 155) almost no light is absorbed. The absorption maxima of dimethyl acetylenedicarboxylate and methyl propiolate lie below the position of the absorption maxima of benzo[b]furan and are weaker. The reaction of benzo[b]furan and the acetylenic esters does not occur in the absence of the sensitizer acetophenone. Thus, as in similar systems,[15] it appears that sensitized formation of the benzo[b]furan triplet state is the initial photochemical act involved in the addition. Charge distribution in the excited benzo[b]furan derives from the direction of addition of the unsymmetrical acetylene (eq 1). The charged excited state of benzo[b]furan might select the carbon of the carboxymethyl group in methyl propiolate.[16,7]

From our results it may be concluded that, by the addition of 1 mol of the acetylene to the benzo[b]furan, a photolabile cyclobutene (IIa,b) is produced (Scheme I). It is obvious that these products must have the cis configuration.[17] In all cases, these cyclobutenes are further converted, by a second light quantum, into a 7-substituted cyclobutene (IIIa,b) which is usually the main product under the conditions used. Rearrangement of IIa,b → IIIa,b likely proceeds via rupture of the

Scheme I



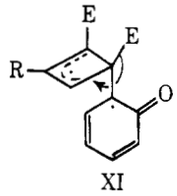
R = CH_3 or H; E = $COOCH_3$

C_1–O bond to give a stabilized diradical X (Scheme I) which can further react to form a new C_6–O bond. This result is in accord with formation of rearranged photoadducts in the reaction of acetylenes with benzo[*b*]thiophene observed in previous studies.[5,7] We suppose that another possibility for the biradical X is that it either forms 1,2-cyclobutenospiro-[2.5]octadienone XII or XIII. Similar intermediates have earlier been postulated in abnormal Claisen rearrangements[18] and in the rearrangement of flavanone.[19] Bond rupture at (a) in XII gives the biradical XI. By bond formation between the original C_5 or C_7 and the oxygen, O, the abnormal rearranged cyclobutenes IVa,b and Va,b arise. With 2-methylbenzo-[*b*]furan the formation of the (possible) photoproducts IIc and IIIc can be similarly explained. The biradical XI (XIV) can also form the spirocyclopropyl intermediate XV (XVI) from which can arise the photoproducts IVc and Vc.

Product distribution derives from the relative stabilities of the biradical intermediates, and polar effects on the ring closures of these intermediates as well as on the steric effects which operate in the ring closure. Thus, IIa,b and Va,b are always minor products because the biradicals leading to their formation are less stable. IIIa,b and IVa,b are major products both because they derive from more stable biradicals and because the polar effects leading to their formation are more favorable.

In all cases the formation of IVa,b (IIc) is preferred over Va,b (IIIc). A reason could be the fact the less steric hindrance of the former compounds. Another reason could be the fact that the intermediate biradical obeys the "principle of least motion".

For getting from the biradical XI into a conformation from which after ring closure products Va,b can arise, there has to be approximately a 90° rotation around the C_{ar}–C_6 axis.



XI

Possibly this rotation is much slower than C_5–O bond formation giving IVa,b.

The rearrangements of the cyclobutenes occur also in the absence of sensitizer, although there is no observed photochemical oxepin formation under these conditions. These reactions are much less efficient than the sensitized process.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded either in chloroform solution or in KBr disks using a Perkin-Elmer 337 infrared spectrophotometer. NMR spectra were recorded on a Varian A-60 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal reference. UV spectra were determined in methanol using a Beckman Acta MIV spectrophotometer. Mass spectra were obtained using a Varian MAT Model CH7 mass spectrometer. Analytical gas–liquid chromatography was carried out using a Varian Aerograph 1200, column 8 ft × 0.125 in., UCON LB 10% on Chromosorb P 60/90. Elemental analyses were performed by Midwest Microlab, Indianapolis, Ind. Photolyses were carried out using a 450-W Hanovia medium-pressure mercury lamp. Samples were contained in sealed 13-mm o.d. Pyrex tubes under nitrogen atmosphere and irradiated on a merry-go-round apparatus immersed in a thermostated water bath (13 ± 1 °C).

Addition of Dimethyl Acetylenedicarboxylate to Benzo-[*b*]furan. A solution of 1.18 g (0.010 mol) of benzo[*b*]furan, 4.45 g (0.032 mol) of dimethyl acetylenedicarboxylate, and 0.24 g (0.002 mol)

of acetophenone in 80 mL of benzene was irradiated for 70 h. After evaporation of the solvent the unreacted benzo[b]furan, the dimethyl acetylenedicarboxylate, and a part of the acetophenone were distilled in vacuo. To prevent rearrangements of the cyclobutene derivatives to the corresponding 1-benzoxepins, one should not use a higher pot temperature than 130 °C. The red-orange colored residue was chromatographed over a Florisil column (100–200 mesh) with CCl_4 as elution agent. Changing solvents carefully from CCl_4 to $CHCl_3$ gave four products, respectively.

1,5-Di(carboxymethyl)-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (Va), yield 1.5%. This product could not be isolated in pure form. The pale yellow oil always contained some of the isomer IVa.

5,6-Di(carboxymethyl)-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (IVa): yield 7%; mp 161–162 °C (methanol); λ_{max} 279 nm (ϵ 2560); NMR δ 3.79 (s, 3 H, $COOCH_3$), 3.82 (s, 3 H, $COOCH_3$), 5.51 (s, H_1), 6.78 (s, H_7), 6.76–7.67 (m, 4 H); IR 1637 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity, fragment) 260 (65), 229 (19, OCH_3), 213 (16), 201 (27, CO_2CH_3), 176 (100, $HC{\equiv}CCO_2CH_3$), 163 (14), 158 (11), 145 (74), 130 (15), 118 (3, $H_3CO_2CC{\equiv}CCO_2CH_3$). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.20; H, 4.68.

1,7-Di(carboxymethyl)-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (IIIa): yield 8%; mp 122–123 °C (methanol; λ_{max} 283 nm (ϵ 2600); NMR δ 3.78 (s, 3 H, $COOCH_3$), 3.88 (s, 3 H, $COOCH_3$), 4.50 (broad s, H_5), 6.78–7.42 (m, 5 H); IR 1633 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity, fragment) 260 (81), 229 (21, OCH_3), 213 (15), 201 (27, CO_2CH_3), 186 (7), 176 (100, $CH{\equiv}CCO_2CH_3$), 163 (10), 158 (10), 145 (79), 130 (13), 118 (19, $H_3CO_2CC{\equiv}CCO_2CH_3$). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.61; H, 4.53.

6,7-Di(carboxymethyl)-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (IIa): yield 9%; oil; NMR δ 3.82 (s, 3 H, $COOCH_3$), 3.84 (s, 3 H, $COOCH_3$), 4.52 and 5.63 (AB, H_5 and H_1, J_{AB} = 3.8 Hz), 6.83–7.51 (m, 4 H); IR 1667 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity, fragment) 260 (65), 229 (23, OCH_3), 213 (8), 201 (23, CO_2CH_3), 186 (8), 176 (6, $HC{\equiv}CCO_2CH_3$), 157 (6), 145 (11), 142 (11), 129 (7), 118 (100, $H_3CO_2CC{\equiv}CCO_2CH_2$). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.80; H, 4.82.

Addition of Dimethyl Acetylenedicarboxylate to 2-Methylbenzo[b]furan. A solution of 6.60 g (0.050 mol) of 2-methylbenzo[b]furan, prepared according to Suu, Buu-Hoi, and Xuong[20] by formation of 2-formylbenzo[b]furan followed by reduction by the Huang-Minlon modification of the Wolff–Kishner reduction, 27.23 g (0.192 mol) of dimethyl acetylenedicarboxylate, and 1.06 g (0.009 mol) of acetophenone in 480 mL of benzene was irradiated for 143 h. The reaction mixture was worked up as described above.

Addition of Methyl Propiolate to Benzo[b]furan. A solution of 3.20 g (0.027 mol) of benzo[b]furan, 6.50 g (0.077 mol) of methyl propiolate, and 0.54 g (0.0045 mol) of acetophenone in 100 mL of benzene was irradiated for 160 h. After evaporation of the unreacted benzo[b]furan, the methyl propiolate and a part of the acetophenone were removed by distillation in vacuo. The dark-colored residue was chromatographed over a Florisil column with $CC_4/CHCl_3$ (7:3) as eluent to give 700 mg of a pale yellow oil. Repeated column chromatography over Florisil with $CCl_4/CHCl_3$ mixtures of increasing ratio as eluent followed by crystallization from methanol gave two products.

6-Carboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (VI): yield 2%; mp 60–61 °C; λ_{max} 279 nm (ϵ 2300); NMR δ 3.82 (s, 3 H, $COOCH_3$), 4.62 and 5.50 (AB, H_5 and H_1, $J_{1,5}$ = 3.8, $J_{5,7}$ = 1.6 Hz), 6.71 (d, H_7), 6.75–7.55 (m, 4 H); IR 1630 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity, fragment) 202 (88), 174 (9, CO), 171 (17, OCH_3), 159 (11, $COCH_3$), 143 (32, $COOCH_3$), 131 (19), 118 (100, $H_3COOCC{\equiv}CH$), 115 (74). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.18; H, 4.95.

1-Carboxymethyl-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene (VII): yield 4%; mp 143–145 °C; λ_{max} 279 nm (ϵ 2400); NMR δ 3.88 (s, 3 H, $COOCH_3$), 4.57 (br s, H_5), 6.23 (q, H_6, $J_{6,7}$ = 2.8, $J_{6,5}$ = 1.2 Hz), 6.82 (d, H_7), 6.77–7.43 (m, 4 H); IR 1635 cm^{-1} (C=C); mass spectrum *m/e* 202.

Photorearrangements of VI and VII. Product VII appeared to be photostable on irradiation for 63 h of a solution of VII in benzene, in the presence of acetophenone as a sensitizer. No rearranged products could be detected by NMR or GC analysis. However, on irradiation of VI for 112 h, VII was obtained (34%) as the only photoproduct.

Thermal Rearrangement of the Di(carboxymethyl)-2-oxabenzo[b]bicyclo[3.2.0]hepta-3,6-diene Derivatives to the Corresponding Di(carboxymethyl)-1-benzoxepins. 4,5-Dicarboxymethyl-1-benzoxepin (IX). IVa (400 mg) was, in its pure form, heated up in an oil bath thermostated at 210 °C for 4 h. After cooling, the dark mixture was chromatographed over Florisil using petroleum ether (bp 20–40 °C)–chloroform (8:2) as eluent, yielding 340 mg (85%) of the benzoxepin IX. After crystallization from methanol an analytical pure sample was obtained: mp 73–74 °C; λ_{max} 297 nm (ϵ 5260); NMR δ 3.87 (s, 3 H, $COOCH_3$), 3.96 (s, 3 H, $COOCH_3$), 6.08 and 6.51 (AB, H_2 and H_3, J_{AB} = 6.0 Hz), 6.95–7.58 (m, 4 H); mass spectrum *m/e* (rel intensity) 260 (100), 229 (33), 217 (26), 201 (31), 176 (21), 163 (26), 158 (21), 145 (30), 142 (10), 130 (31), 118 (76). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.90; H, 4.58. Upon irradiation of a solution of IX in benzene for 65 h, compound IVa was obtained in 85% yield, with the same spectroscopic and physical data as described above.

2,3-Dicarboxymethyl-1-benzoxepin (VIII). IIIa (150 mg) was treated in the same way as described above at 185 °C for 1 h. The dark residue was purified by column chromatography over Florisil using petroleum ether–chloroform (8:2) as eluent, yielding 122 mg (81%) of the benzoxepin VIII: mp 67–68 °C (methanol); λ_{max} broad absorption maximum in the 302–330-nm region with two distinct absorption maxima at 306 and 328 nm (ϵ 3700); NMR δ 3.84 (s, 3 H, $COOCH_3$), 3.91 (s, 3 H, $COOCH_3$), 6.39 and 7.06 (AB, H_4 and H_5, J_{AB} = 11, 5 Hz), 7.07–7.60 (m, 4 H); mass spectrum *m/e* (rel intensity) 260 (100), 232 (20), 229 (25), 217 (12), 201 (28), 185 (27), 170 (20), 157 (26), 145 (41), 130 (22), 129 (23), 118 (83). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.58; H, 4.64. Upon irradiation of a solution of VIII in benzene for 65 h, compound IIIa was obtained (and some traces of IVa) with the same spectroscopic and physical data as described above.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors thank Professor Thomas H. Kinstle for the mass spectral data recorded.

Registry No.—Ia, 271-89-6; Ib, 4265-25-2; VIII, 62250-85-5; IX, 62250-86-6; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8.

References and Notes

(1) Fellow of the Alfred P. Sloan Foundation, 1971–1976.
(2) M. V. George, S. K. Khetan, and R. K. Gupta, *Adv. Heterocycl. Chem.*, **19**, 279 (1976).
(3) M. S. Lin and V. Snieckus, *J. Org. Chem.*, **36**, 645 (1971).
(4) D. N. Reinhoudt and C. G. Kouwenhoven, *Tetrahedron Lett.*, 5203 (1972).
(5) D. N. Reinhoudt and C. G. Kouwenhoven, *Tetrahedron*, **30**, 2431 (1974).
(6) W. H. F. Sasse, P. J. Collin, and D. B. Roberts, *Tetrahedron Lett.*, 4791 (1969).
(7) J. H. Dopper and D. C. Neckers, *J. Org. Chem.*, **36**, 3755 (1971).
(8) The most general mechanism of oxetane formation involves addition of $n{-}\pi^*$ excited-triplet carbonyl compounds to ground-state olefins having higher triplet excitation energies than that of the adding carbonyl compound.[9] Cf. (a) C. H. Krauch, W. Metzner, and G. O. Schenck, *Chem. Ber.*, **99**, 1723 (1966); (b) S. Farid and S. E. Shealer, *J. Chem. Soc., Chem. Commun.*, 296 (1973); (c) Y. Kawase, S. Yamaguchi, H. Ochiai, and H. Horita, *Bull. Chem. Soc. Jpn.*, **47**, 2660 (1974); (d) S. Farid, S. E. Hartman, and C. D. deBoer, *J. Am. Chem. Soc.*, **97**, 808 (1975).
(9) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).
(10) D. C. Neckers, J. H. Dopper, and H. Wynberg, *J. Org. Chem.*, **35**, 1582 (1970).
(11) (a) T. W. Doyle, *Can. J. Chem.*, **48**, 1629, 1633 (1970); (b) R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, **102**, 3444 (1969).
(12) (a) These data do not agree with the chemical shifts of H_2 and H_3 found in the NMR spectrum of 4,5-dicarboxymethyloxepin, δ 5.06 and 6.27 ppm (AB, J_{AB} = 5.0 Hz): H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem., Int. Ed. Engl.*, **5**, 1039 (1966). However, they are in good agreement with the chemical shifts of the vinylic protons in several substituted 1-benzoxepins. Cf. (b) H. Hofmann and H. J. Haberstroh, *Justus Liebigs Ann. Chem.*, 2032 (1973); (c) H. Hofmann and P. Hofmann, *ibid.*, 1301 (1974); (d) *Chem. Ber.*, **106**, 3571 (1973).
(13) L. A. Paquette and J. H. Barett, *J. Am. Chem. Soc.*, **88**, 1718 (1966); J. M. Holovka and P. D. Gardner, *ibid.*, **89**, 6390 (1967); E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); H. Hofmann and P. Hofmann, *Tetrahedron Lett.*, 4055 (1971); H. Hofmann and B. Meyer, *ibid.*, 4597 (1972).
(14) DMS UV Atlas, Vol. V, H 4/1.
(15) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, **30**, 1849 (1965); P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Rev. Pure Appl. Chem.*, **16**, 187 (1968).
(16) R. Huisgen, H. Golhard, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968).
(17) R. P. Ghandi and V. K. Chadka, *Indian J. Chem.*, **6**, 402 (1968).
(18) A. T. Shulgin and H. O. Kerlinger, *Tetrahedron Lett.*, 3355 (1965); C. M. Orlando and H. Mark, *ibid.*, 3003 (1966); C. M. Orlando, H. Mark, A. K. Bose, and M. S. Manhas, *J. Org. Chem.*, **33**, 2512 (1968); E. N. Marbell and B. Schats, *Tetrahedron Lett.*, 67 (1970); S. Farid, *Chem. Commun.*, 303 (1970); E. Schmid, G. Frater, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 1625 (1972).
(19) P. O. L. Mack and J. T. Pinhey, *J. Chem. Soc., Chem. Commun.*, 451 (1972).
(20) V. T. Suu, N. P. Buu-Hoi, and N. D. Xuong, *Bull. Soc. Chim. Fr.*, 1875 (1962).