PHOTOCHEMICAL ORGANIC SYNTHESES—I

PHOTOCHEMICAL ADDITION OF FORMAMIDE AND ANILINE TO CROTONIC ACID AND ITS ESTERS[1]

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Abstract—In light-induced amidation of crotonic acid and its esters with formamide, yields of 60–77% of the 1-1-adducts were obtained. The distribution of the isomers of the 1-1-adducts was found to differ in the case of acid and ester. For example, crotonic acid yielded 2-, 3-, and 4-carbamoylbutyric acid in a ratio of 41:28:31, whereas in methyl crotonate the corresponding distribution was 8:41:51. It was confirmed that the γ-adduct is obtained by an addition reaction of formamide with the β,γ-unsaturated acid or ester produced by photoisomerization of the corresponding αβ-unsaturated compounds. The photoisomerization of crotonic acid and its esters was studied under varying conditions.

A photochemical addition of aniline to crotonic acid and its esters gave different yields and distributions according to the conditions used. But it was found that the acid yields essentially a pure β-adduct, while the esters give an α-adduct as the main product.

FREE-radical addition reactions to olefins are widely known.[3] Various workers have also reported on the photochemical reaction of α,β-unsaturated ketones[4] including the addition reaction, but photochemical additions to α,β-unsaturated acids and their derivatives have not been checked systematically. It has been established that, where steric factors do not intervene, the course of a homolytic reaction depends on the relative stability of the intermediate free radical involved[5] and many papers dealing with the stabilizing influences of substituents on free alkyl radicals have been published.[6] On the other hand, steric effects[7] such as B strain and I strain in free radical reactions must be taken into account and in addition, the "orientation effect", must be considered. For example, if a radical interacts with part of an olefin such as hydrogen bonding, the attack of the radical on the olefin appears restricted. Consequently, such a steric factor could change the directive effect of radical addition to the double bond.

In order to examine the various steric effects, a study on the addition of formamide and aniline to crotonic acid and its esters was undertaken.

RESULTS AND DISCUSSION

Addition of formamide. In a radical addition to α,β-unsaturated carbonyl compounds, it has been reported that β-addition is more favorable than α-addition, because of the stability of the intermediate radical. For instance, the photochemical reaction of aniline with crotonic acid[8] yields only β-anilinobutyric acid and β-anilinobutyranilide and the addition of aldehydes to mesityl oxide[9] initiated by benzoylperoxides gives α- and β-adducts in a ratio of 1:10. Recently, Elad *et al.*[10] reported that the light-induced addition of formamide to α,β-unsaturated esters produces only the β-adduct.
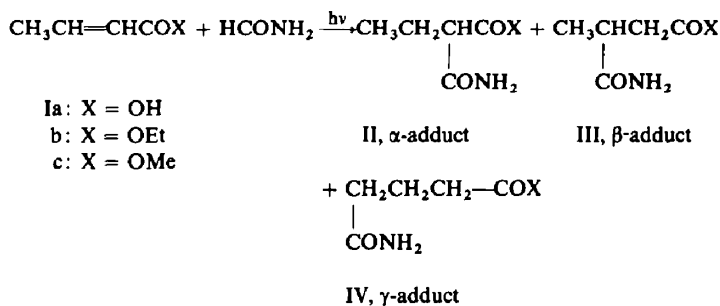
The light-induced additions of formamide to crotonic acid (Ia), ethyl ester (Ib)

and methyl ester (Ic) were carried out in t-butanol solution with acetone as a sensitizer using a 150 W high pressure mercury vapor lamp for 100 hr. The results are summarized in Table 1.

TABLE 1. PHOTOCHEMICAL ADDITION OF FORMAMIDE TO CROTONIC ACID AND ITS ESTERS

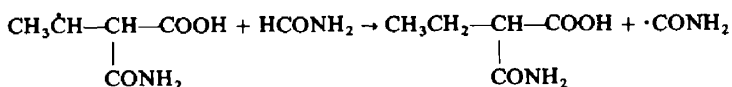| Substrate	Yield of 1:1-adduct %[a]	Distribution of products		
		α-Adduct (II)	β-Adduct (III)	γ-Adduct (IV)
$CH_3CH=CHCO_2H$	60	41	28	31
$CH_3CH=CHCO_2Et$	68	10	48	42
$CH_3CH=CHCO_2Me$	77	8	41	51

[a] Based on crotonic acid and its esters employed.

$$CH_3CH=CHCOX + HCONH_2 \xrightarrow{h\nu} CH_3CH_2CHCOX + CH_3CHCH_2COX$$

$$| \qquad\qquad |$$
$$CONH_2 \qquad CONH_2$$

Ia: X = OH
 b: X = OEt
 c: X = OMe

II, α-adduct　　　III, β-adduct

$$+ CH_2CH_2CH_2—COX$$
$$|$$
$$CONH_2$$

IV, γ-adduct

As indicated, the light-induced amidation of crotonic acid and its esters gave 1:1-adducts in the yield of 60 to 77%, but the distributions of the product isomers were not identical. As suggested, an important factor controlling the direction of addition to α,β-unsaturated carbonyl compounds is the stability of the intermediate radical.[3, 5, 6, 9] Consequently, β-addition is more favorable in α,β-unsaturated carbonyl compounds, because the intermediate radical seems to be stabilized by resonance.

The light-induced addition of formamide to crotonic esters provided α- and β-adducts in the approximate ratio of 1:5, but in the case of crotonic acid itself, the ratio was 3:2. The result could be explained as follows. In the amidation of olefins with formamide, it appears that carbamoyl radicals ·$CONH_2$ are generated in the mixture either as a result of the collapse of the photoactivated formamide molecule or by hydrogen atom abstraction from formamide by other radicals formed.[11] The carbamoyl radical thus obtained may form a hydrogen bond between its carbonyl oxygen and the hydroxyl hydrogen of crotonic acid prior to the attack of the radical to the α,β-unsaturated double bond. The intermediate V would produce the α-adduct as a main product, because the formation of a 6-membered ring transition state is easier than a 7-membered ring transition state.[12, 13] Such a hydrogen bond would not be expected in crotonic acid esters.

The γ-adduct (IV) was obtained in a yield of 18 to 39%. The formation may be elucidated as follows. After *trans*-crotonic acid (VI) isomerizes to the *cis*-isomer (VII) under the influence of UV light, the n–π* excited carbonyl oxygen of the *cis*-isomer

$$H—CONH_2 \xrightarrow{h\nu} \cdot CONH_2$$

$$CH_3—CH{=}CHCOOH + \cdot CONH_2 \rightarrow CH_3—CH{=}CH$$

V

$$V \rightarrow CH_3\overset{\cdot}{C}H—CH—COOH$$
$$|$$
$$CONH_2$$

$$CH_3\overset{\cdot}{C}H—CH—COOH + HCONH_2 \rightarrow CH_3CH_2—CH—COOH + \cdot CONH_2$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad CONH_2 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CONH_2$$
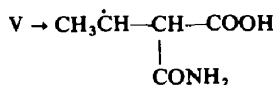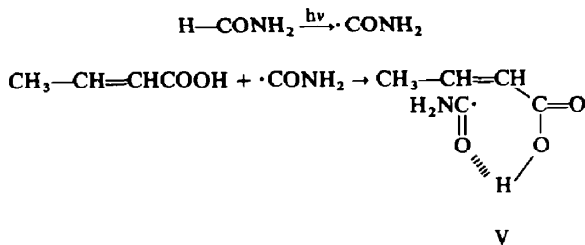
abstracts a hydrogen atom from the γ-carbon,[14, 15] and the β,γ-isomer (VIII) is obtained via an enol form.

VIa: X = OH
b: X = OEt
c: X = OMe

VII

VIII

IV

(A)
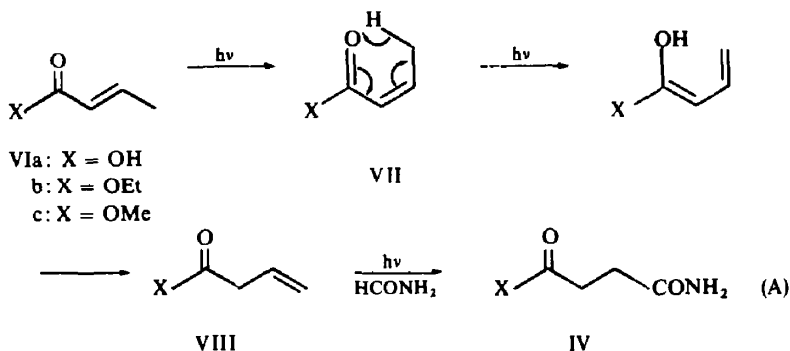
The addition of a carbamoyl radical to the γ-position of the β,γ-unsaturated isomer (VIII) may give the γ-adduct (IV).

In order to confirm whether the β,γ-isomer is actually produced in the reaction, *trans*-crotonic acid and its ethyl ester were treated under the same conditions in the absence of formamide. The results are shown in Table 2. The irradiation of *trans*-crotonic acid and its esters gave the mixture of *trans*-VI, *cis*-VII and the β,γ-isomer (VIII).

VIa: X = OH
b: X = OEt

VI

VII
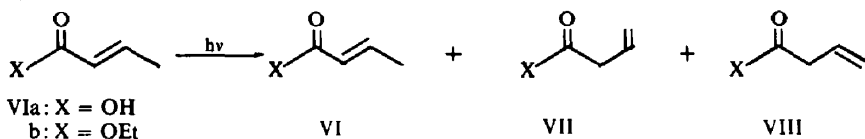
VIII

When *cis*-ethyl crotonate (VIIb) was irradiated at a low concentration, the *cis*-isomer was found to isomerize completely to the β,γ-isomer (VIIIb). Irradiation of the β,γ-unsaturated ester (VIIIb) gave no change. On the other hand, when *trans*-ethyl crotonate (VIb) was irradiated in methanol solution with light of wavelengths above 300 mμ (Pyrex filter), no isomerization was observed. Irradiation with low pressure

Table 2. Photoisomerization of crotonic acid and its ester

Substrate	Solvent	Light[a] Source	Distribution of products			
			Reaction time (hr)	trans- (VI)	cis- (VII)	β,γ- (VIII)
trans-CH₃CH=CHCO₂Et	t-BuOH[b]	HPL	45	38	27	35
	MeOH	HPL	20	34	30	36
	MeOH	HPL-P	40	100	0	0
	MeOH	LPL	30	73	25	2
	Benzene	HPL	40	85	15	0
cis-CH₃CH=CHCO₂Et	t-BuOH[b]	HPL	12	0	0	100
trans-CH₃CH=CHCO₂H	t-BuOH[b]	HPL	30	48	28	24
	Benzene	HPL	40	93	7	0

[a] HPL: 500 W high pressure mercury vapor lamp, HPL-P: 500 W high pressure mercury vapor lamp surrounded by a Pyrex jacket, LPL: 15 W low pressure mercury vapor lamp.

[b] Mixed with acetone.

mercury vapor lamp was not effective for the purpose of isomerization to the β,γ-isomer, probably because light for n–π* excitation was not emitted. The distribution of the three isomers obtained in these isomerizations seem to be influenced by the solvent, concentration of the substrate, and the reaction temperature. The isomerization appears to be affected by the light of wavelengths under 300 mμ.

Light-induced amidation of formamide to ethyl vinylacetate (VIIIb) in the presence of acetone as a sensitizer in t-butanol solution provided a mixture of 1:1-adducts in a yield of 66%, which consists of 93% γ-adduct and 7% β-adduct. Under similar conditions, amidation of ethyl crotonate (VIb) gave a mixture of 1:1-adducts in a yield of 50%. This means that formamide adds more rapidly to a terminal double bond than to an inner double bond. Consequently, the experimental results mentioned above, confirm that the γ-adduct is formed by the reaction path described in Equation A.

$$CH_2=CHCH_2CO_2Et + H-CONH_2 \xrightarrow{h\nu} CH_2CH_2CH_2CO_2Et + CH_3CHCH_2CO_2Et$$

$$\underset{CONH_2}{|} \qquad\qquad \underset{CONH_2}{|}$$

VIIIb   IVb   IIIb

Recently, various photochemical isomerizations of α,β-unsaturated compounds to β,γ-unsaturated isomers have been reported; for instance, photoisomerizations of phorone,[16] substituted methyl vinyl ketones,[14, 17a,][18] 1-acethylcyclohexene,[17] sorbic acid,[19] ortho-substituted benzophenone,[20] crotonaldehyde‡ and others.[22]

Most of the photoenolizations seem to proceed via the 6-center mechanism given for cis-crotonate (Eq. A), but some cases[17, 22c] are known in which photoenolization cannot be expected to proceed via such a mechanism, because of the structural

† In recent experiments using highly purified solvents, the isomerization of 1-acetoxycyclohexene to 3-acetylcyclohexene does not appear to occur.[17b]

‡ The photolysis of crotonaldehyde in the gas phase was carried out at 30° using the light with the wave length between 2450–4000 Å and yielded CO, propylene 1,5-hexadiene and 3-buten-2-al.[21] It was reported that this unsaturated aldehyde is obtained by the primary process of this photolysis.
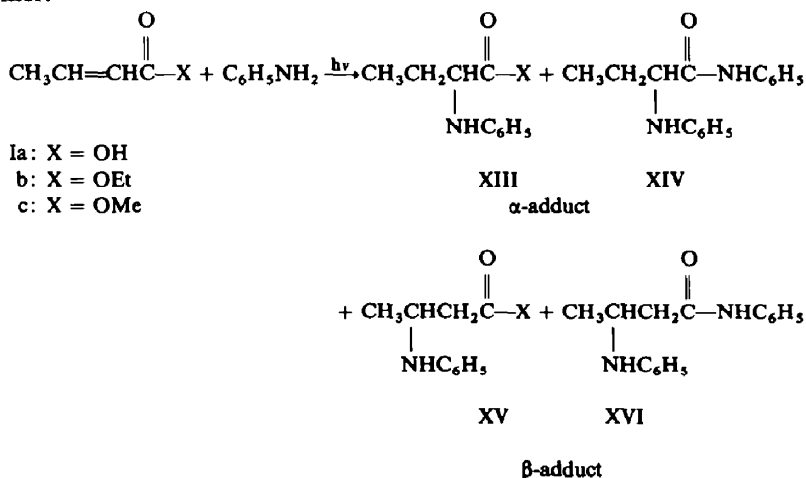
requirement. In the case of mesityl oxide (XI), it has been reported that photoiso-merization does not occur in spite of the satisfactory structural environment.[14, 15] Methyl propenyl ketone (XII) likewise does not photoisomerize under similar conditions.[14, 23] Since ethyl β,β'-dimethyl acrylate (IX) resembles mesityl oxide (XI) structurally and electronically, we attempted the photoisomerization of IX. When the ester was irradiated in t-butanol with UV light, the β,γ-unsaturated isomer (X) was obtained in a yield of 50% after 50 hr, 64% after 100 hr and 73% after 150 hr.

$$\text{IX} \xrightarrow{h\nu} \text{X}$$

$$\text{XI} \xrightarrow{h\nu} \text{no reaction}$$

$$\text{XII} \xrightarrow{h\nu} \text{no reaction}$$
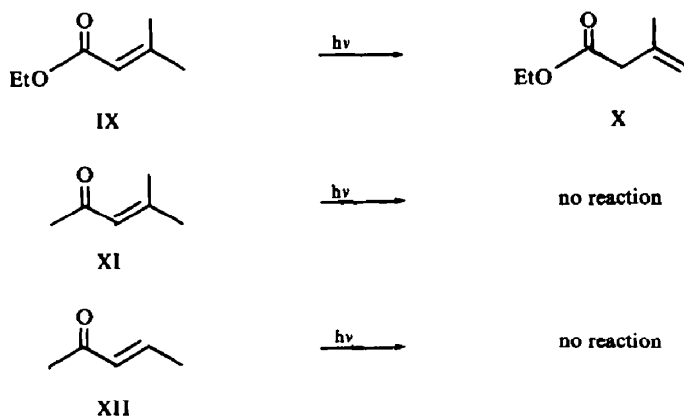
The reactivity changes in various α,β-unsaturated ketones have been discussed[14, 15] but no definite conclusion has been reached. The difference in the reactivity between the α,β-unsaturated esters and the ketones requires further examination and the work is in progress in this laboratory.

Addition of aniline. The reaction of crotonic acid and anailine under UV light irradiation gave only β-addition products, β-anilinobutyric acid (XVa) and β-anilino-butyranilide (XVIa) in a yield of 60% and 11%, respectively. Irradiation of a mixture of crotonic acid ester and aniline yielded α- and β-adducts with a preponderance of the former.

$$CH_3CH{=}CHC{-}X + C_6H_5NH_2 \xrightarrow{h\nu} CH_3CH_2\underset{\underset{NHC_6H_5}{|}}{C}HC{-}X + CH_3CH_2\underset{\underset{NHC_6H_5}{|}}{C}HC{-}NHC_6H_5$$

Ia: X = OH
b: X = OEt
c: X = OMe

XIII   XIV
α-adduct

$$+ CH_3\underset{\underset{NHC_6H_5}{|}}{C}HCH_2C{-}X + CH_3\underset{\underset{NHC_6H_5}{|}}{C}HCH_2C{-}NHC_6H_5$$

XV   XVI
β-adduct

The yields of 1:1-adducts and distribution of α- and β-adducts are summarized in Table 3. When a solution of crotonic acid and aniline in benzene was irradiated

TABLE 3. PHOTOCHEMICAL ADDITION OF ANILINE TO CROTONIC ACID AND ITS ESTERS

Substrate	Light[a] Source	Solvent	Yield of 1:1-adduct %[b]	Distribution of products	
				α-Adduct	β-Adduct
$CH_3CH{=}CHCO_2H$	HPL	Benzene	71	0	100
	LPL	Benzene	16	0	100
	HPL-P	Benzene	<1	0	100
	HPL	t-BuOH	8	0	100
$CH_3CH{=}CHCO_2Et$	HPL	Benzene	9	62	38
	HPL	Benzene[c]	14	64	36
	LPL	Benzene	2	70	30
$CH_3CH{=}CHCO_2Me$	HPL	Benzene	6	62	38

[a] HPL: 150 W high pressure mercury vapor lamp, LPL: 15 W low pressure mercury vapor lamp, HPL-P: 500 W high pressure mercury vapor lamp surrounded by a Pyrex jacket.

[b] Based on crotonic acid and its esters employed.

[c] Added with acetone.

with light of wavelengths exceeding 300 mµ (Pyrex filter), the yield of the 1:1-adduct was decreased. Irradiation with a low pressure lamp produced the adduct in 16% yield. When t-butyl alcohol was used as a solvent, the yield of 1:1-adduct was lowered from 71% to 8%. In the case of ethyl crotonate, the yield was retarded, when a low pressure lamp was used. With added acetone, the yield was raised slightly.

On the basis of these results, benzene was found to act as a sensitizer in the reaction, suggesting the presence of two kinds of excitations; direct excitation of aniline and indirect excitation by an energy transfer from benzene.† Light below 300 mµ seems to be more effective in this reaction, especially between 260 mµ of benzene absorption and 280 mµ of the aniline absorption band.

In the photochemical addition of aniline to crotonic acid and its esters, no γ-adduct was obtained. This is explained by the experimental fact that irradiation of crotonic acid ester gives no β,γ-unsaturated isomer in benzene solution. In addition, it was also confirmed that no product was obtained in the reaction of ethyl vinylacetate (VIIIb) and aniline with UV light.

In the irradiation of crotonic acid ester and aniline, the preponderance of the α-adduct may be explained by the following mechanism. It is known that the anilino radical is produced in UV irradiation of aniline.[24] Then, electron transfer[25] may occur between the anilino radical and the crotonic acid ester as described in Equation B. The anilino cation (XVII) formed has resonance structures such as XVIII and XIX. When an electron deficient ortho-carbon of the structure XVIII approaches the electron rich carbonyl oxygen, the α-carbon of ethyl crotonate becomes susceptible to an attack by the N atoms of aniline through a 6-membered ring transition state (XX).

Consequently, the α-adduct appears as the main product. Such an electron transfer would not occur in the case of crotonic acid itself, because the acid appears to exist as the ion pair, $RCOO^- \cdot PhNH_3^+$ in the solution, and only the β-adduct would be

† Triplet states of benzene and aniline are 85 and 77 kcal/mole repsectively. If this reaction is assumed to proceed via triplet state, triplet–triplet transfer from excited benzene is possible to occur.

produced according to the usual manner of radical addition. It is very interesting that irradiation of crotonic acid and aniline gives 1:1-adducts in higher yield than that of its ester, but the difference cannot be explained at present.

(B)

XVII   XVIII   XIX

XX
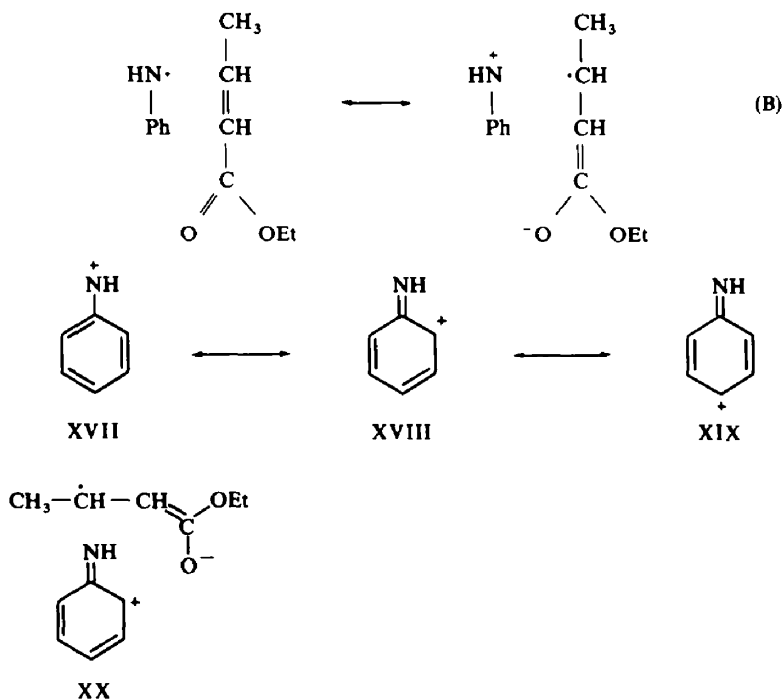
EXPERIMENTAL

All m.ps and b.ps are uncorrected. GLPC analysis was taken with a Yanagimoto Model GCG-220 (H_2 as carrier gas) and a Hitachi KGL-2A (using a capillary column, H_2 as carrier gas), for preparative work with a Wilkens Autoprep 700 (N_2 as carrier gas). IR spectra were obtained with a Hitachi EPI-2A, and NMR spectra were measured with a Nihon Denshi 3H-60 (TMS as an internal standard). Light sources used were as follows; 150 W and 500 W high pressure mercury vapor lamp with a water cooling quartz jacket (150 W HPL and 500 W HPL), 500 watt high pressure mercury vapor lamp with a water cooling Pyrex jacket (500 W HPL-P) and 15 W low pressure mercury vapor lamp (15 W LPL).

Photochemical addition of formamide to ethyl crotonate. Experiments were conducted in an immersion apparatus using 150 watt HPL. The reaction mixture was cooled externally with water and agitation was achieved by a magnetic stirrer. N_2 was passed through the mixture throughout the reaction. All reagents were freshly distilled and recrystallized before use.

A mixture of ethyl crotonate (0·1 mole), formamide (1·5 mole), acetone (0·2 mole) and t-BuOH (400 ml) was irradiated for 100 hr. After filtration of oxamide (605 mg) and removal of solvent, unreacted ethyl crotonate, acetone and formamide, the residue was redissolved in hot acetone. An insoluble solid, 30 mg of oxamide, was reseparated. Thus 12·5 g (75%) of the crude product was obtained. The crude product was hydrolysed with 6N NaOH for 10 hr and then esterified with EtOH† in the presence of H_2SO_4. GLPC analysis (Apiezon grease L 20% coated on Diasolid L; 170°) of the esterified product indicated the presence of four peaks in a ratio of 9:41:36:14. The former three were separated by using a preparative GLPC machine (Apiezon grease L, 190°). Peak 1, n_D^{20} 1·4170. (Found: C, 57·62; H, 8·44; mol wt, 188.‡ Peak 2,

† As the peak of ethyl butyrate did not appear in the GLPC analysis of the esterified products, possibly no decarboxylation occurred during hydrolysis.

‡ Molecular weights were determined by mass spectroscopic method.

n_D^{20} 1·4189; Found: C, 57·19; H, 8·63; mol wt, 188. Peak 3, n_D^{20} 1·4240; Found: C, 57·48; H, 8·58; mol wt, 188. Calc. for $C_9H_{16}O_4$: C, 57·43; H, 8·57%).

The compounds were identified as diethyl ethylmalonate, diethyl methylsuccinate and diethyl glutarate by comparison with authentic samples which were prepared by Wallingford's,[26] Wojeik's[27] and Marvel's[28] procedures, respectively. The forth peak was not identified. The yield of 1:1-adduct was calculated as 68% on the base of ethyl crotonate used.

Photochemical addition of formamide to methyl crotonate. A mixture of methyl crotonate (0·1 mole), formamide (1·5 mole), acetone (0·2 mole) and BuOH (350 ml) was irradiated for 100 hr. Treatment of a reaction mixture gave 2·3 g of oxamide and 9·2 g of the crude product. Upon the GLPC analysis after esterification, four peaks appeared in the ratio of 35:24:27:14 and the former three corresponded α-, β- and γ-adduct. Therefore, the distribution of α-, β- and γ-adduct in 1:1-adduct was 41, 28 and 31%, respectively. The yield of 1:1-adducts was calculated as 60%.

Photochemical addition of formamide to ethyl vinylacetate. Ethyl vinylacetate was prepared by the method described by Rietz.[29]

A mixture of ethyl vinyl acetate (0·05 mole), formamide (0·75 mole) acetone (0·10 mole) and t-BuOH (170 ml) wa irradiated for 20 hr with a 150 W HPL. A crude product, amounting to 5·7 g, was thus obtained. GLPC analysis of the esterified product indicated the presence of three components in a ratio of 6:86:8 and the former two were found to correspond β- and γ-adduct. The third was not identified. The distribution of β- and γ-adduct in 1:1-adducts was, therefore, 7 and 93%. The yield of 1:1-adducts was calculated as 66%.

Similarly, a mixture of ethyl crotonate (0·05 mole), formamide (0·75 mole) acetone (0·10 mole) and t-BuOH (170 ml) was irradiated for 20 hr, from which 4·6 g of crude product was obtained. The yield of 1:1-adducts was 50%.

Photochemical isomerization of trans-ethyl crotonate (VIb). A mixture of ethyl crotonate (0·025 mole), acetone (0·005 mole) and t-BuOH (40 ml) in a cylindrical quartz reaction cell (20 × 250 mm) was irradiated with a 500 W HPL. The reaction mixture was cooled externally with water, and N_2 was passed through the mixture throughout the irradiation. Periodically, aliquots were withdrawn and analysed by GLPC. After irradiation was continued for 45 hr, GLPC analysis indicated the presence of three peaks in a ratio of 35:27:38. The distribution of three components was also confirmed by NMR analysis, which indicated no isomerization of each component in the column of GLPC. Three components were fractionated by preparative GLPC (Apiezon grease L, 105°), The first, n_D^{20} 1·4102, was found to be VIIIb by comparison with authentic sample.[29] (Found: C, 63·03; H, 8·65. Calc. for $C_6H_{10}O_2$: C, 63·13; H, 8·83%).

The second, n_D^{20} 1·4241, was determined as cis-VIIb by the following spectroscopic data:[30] IR, 3040 ($v_{=C-H}$), 2970, 1720 ($v_{C=O}$), 1640 ($v_{C=C}$), 1435 ($v_{=C-H}$), 1360, 1280, 1245, 1185 (v_{-C-O}), 1030, 950, 815 ($\delta_{=C-H}$) cm^{-1}; NMR in τ, a triplet at 8·72 (3H), a quartet at 7·85 (3H, $J = 7·5$ c/s, $J = 1·5$ c/s), a quartet at 5·88 (2H), a doublet at 4·31 (1H, $J = 12$ c/s) and a multiplet at 3·75 (1H). (Found: C, 62·93; H, 8·71. Calc. for $C_6H_{10}O_2$: C, 63·13; H, 8·83%).

The third was the starting material VIb. Its spectral data are as follows: IR, 3060 ($v_{=C-H}$), 2970, 1720 ($v_{C=O}$), 1665 ($v_{C=C}$), 1440, 1365, 1308, 1265, 1185 (v_{-C-O}), 1103, 1060, 970 ($\delta_{=C-H}$), 840 cm^{-1}; NMR in τ, a triplet at 8·72 (3H), a quartet at 8·08 (3H, $J = 7·5$ c/s, $J = 1·5$ c/s), a quartet at 5·86 (2H), a doublet at 4·23 (1H, $J = 15$ c/s) and a multiplet at 3·10 (1H).

When a soln of trans-ethyl crotonate in MeOH was irradiated for 25 hr with a 500 W HPL, VIb, VIIb and VIIIb were obtained in a ratio of 34:30:36.

After irradiation of the ester in MeOH for 40 hr with a 500 W HPL-P, no detectable change was observed upon GLPC analysis.

When a soln of trans-ethyl crotonate in MeOH was irradiated for 30 hr with a 15 W LPL, VIb, VIIb and VIIIb were obtained in a ratio of 73:25:2.

Photochemical isomerization of cis-ethyl crotonate (VIIb) cis-Ethyl crotonate was obtained by preparative GLPC (Apiezon grease L, 105°) from the irradiated soln of trans-ethyl crotonate. A mixture of cis-ethyl crotonate (0·01 mole), acetone (0·002 mole) and t-BuOH (160 ml) was irradiated for 20 hr with a 150 W HPL. GLPC analysis indicated a complete isomerization of VIIb to VIIIb.

Photochemical isomerization of ethyl vinylacetate (VIIIb). A mixture of ethyl vinylacetate[29] (0·1 mole), acetone (0·02 mole) and 5-BuOH (150 ml) was irradiated with a 150 W HPL. Ethyl vinylacetate was found to be unreactive after irradiation for 25 hr.

Photochemical isomerization of trans-crotonic acid (VIa). A mixture of trans-crotonic acid (m.p. 72·0–72·5°, 0·05 mole), acetone (0·01 mole) and t-BuOH (40 ml) was irradiated with 500 W HPL. As a suitable column of GLPC was not found for isomeric crotonic acids, the analysis was carried out by NMR. The

NMR spectrum of the mixture in CCl_4 indicated that the Me group of *trans*-crotonic acid appears at τ 8·04, the Me group of *cis*-crotonic acid at 7·74 and the methylene group of vinyl acetic acid at 6·85. A ratio of *trans*-VIa, *cis*-VIIa and β,γ-isomer VIIIa was determined from the peak areas. After irradiation was continued for 30 hr, VIa, VIIa and VIIIa were obtained in a ratio of 48:28:24, respectively.

A soln of crotonic acid (0·1 mole) in benzene (170 ml) was irradiated for 40 hr with a 150 W HPL. The NMR data in benzene were as follows: Me group of VIa at τ 8·67, Me group of VIIa at 8·07, and methylene group of VIIIa at 7·23. In this case, 7% of *trans*-crotonic acid was converted to *cis*-isomer and no β,γ-isomer was found.

Photochemical isomerization of ethyl β,β′-dimethylacrylate (IX). Ethyl β,β′-dimethylacrylate was prepared according to the direction of Smith *et al.*[31] The spectral data of XIII are as follows: IR, 2960, 1715, 1655, 1440, 1375, 1225, 1150, 1080, 1030, 850 cm^{-1}; NMR spectrum in CCl_4, a triplet at τ 8·73 (3H), a doublet at 8·09 (3H, J = 1·5 c/s), a doublet at 7·83 (3H, J = 1·5 c/s), a quartet at 5·90 (2H) and a multiplet at 4·38 (1H. J = 1·5 c/s).

A mixture of ethyl β,β′-dimethylacrylate (0·05 mole), acetone (0·01 mole) and t-BuOH (150 ml) was irradiated for 150 hr with 150 W HPL. GLPC analysis (Squarane capillary column 90 m, 120°) showed the presence of a isomeric product, which was separated with preparative GLPC (Apiezon grease L, 120°). It was found to be β,γ-unsaturated isomer, X; IR, 3070, 2960, 1735, 1650, 1440, 1365, 1160, 1040, 890 cm^{-1}. NMR in CCl_4, a triplet at τ 8·72 (3H), a singlet at 8·16 (3H), a singlet at 7·00 (2H) a quartet at 5·87 (2H) and a multiplet at 5·14 (2H). (Found: C, 65·46; H, 9·35. Calc. for $C_7H_{12}O_2$: C, 65·59; H, 9·44%).

Photochemical addition of aniline to crotonic acid. A mixture of crotonic acid (10·0 g), aniline (20·0 g) and benzene (400 ml) was irradiated for 72 hr with a 150 W HPL. Treatment of the reaction mixture was carried out by the procedure reported by Stoermer[6] which gave 3·0 g (11%) of XVI and 12·9 g (60%) of XVa. These compounds were characterized by comparison with the authentic samples of their hydrochlorides.[32]

A mixture of crotonic acid (0·1 mole), aniline (0·2 mole) and benzene (300 ml) was irradiated for 72 hr with a 15 W LPL. Treatment of the reaction mixture gave 0·4 g of XVI (yield, 2%) and 2·4 g of XVa (yield, 14%).

A mixture of crotonic acid (0·1 mole), aniline (0·2 mole) and benzene (300 ml) was irradiated for 50 hr with a 500 W HPL-P, which gave only a trace of XVI and β-XVa.

A mixture of crotonic acid (0·1 mole), aniline (0·2 mole) and t-BuOH (180 ml) was irradiated for 72 hr with a 150 W HPL, and a mixture of 0·8 g of XVI (yield, 3%) and 0·9 g of XVa (yield, 5%) was produced.

Photochemical addition of aniline to ethyl crotonate. A mixture of ethyl crotonate (0·1 mole), aniline (0·2 mole) and benzene (340 ml) was irradiated for 72 hr with a 150 W HPL. After removal of unreacted reagents and the solvent, 3·1 g of the crude product was obtained. This was fractionated at 2 mm to give 2·0 g of the distillate (116–130°). GLPC analysis (Apiezon grease L 20% coated on Diasolid L, 255°) of the distillate indicated the presence of XIIIb and XVb in a distribution of 62:38, and identified by comparison with the authentic samples. Ethyl α-anilinobutyrate was prepared by the reaction of α-bromobutyrate and aniline.[33] Thus, the yield of 1:1-adduct was calculated as 9% on the bases of ethyl crotonate.

A mixture of ethyl crotonate (0·1 mole), aniline (0·2 mole), acetone (0·1 mole) and benzene (300 ml) was irradiated for 50 hr with a 500 W HPL. By treating the reaction mixture as described above, 3·1 g of a distilled fraction was obtained. The yield of 1:1-adduct was calculated as 14% and the distribution of α- and β-adduct was found to be 64 and 36% by GLPC analysis.

A mixture of ethyl crotonate (0·1 mole), aniline (0·2 mole) and benzene (250 ml) was irradiated for 72 hr with a 15 W LPL. Two per cent of 1:1-adduct (0·5 g) was obtained and the distribution of α- and β-adduct was 70 and 30%.

Photochemical addition of aniline to methyl crotonate. A mixture of methyl crotonate (0·1 mole), aniline (0·2 mole) and benzene (350 ml) was irradiated for 72 hr with a 150 W HPL, and then 1·2 g of 1:1-adduct (yield: 6%) was obtained and the distribution of α- and β-adduct was 62:38.

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