"doublet" at τ 6.11 and 6.25, whereas even unsymmetrically substituted polymethyldiphenylmethanes[18] show only one peak for the CH_2 group. Apparently, therefore, the isomeric mixture was more complex than indicated by gas chromatography.

(18) High Resolution NMR Spectra Catalog by Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 357.

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.72; H, 9.45.

Acknowledgments.—The authors are indebted to S. Meyerson, E. M. Banas, R. R. Hopkins, and D. K. Albert, all of American Oil Co., for the spectroscopic and gas chromatographic analyses.

Photoamidation. IV.[1] The Light-Induced Amidation of α,β-Unsaturated Esters

JOSHUA ROKACH[2] AND DOV ELAD

Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth, Israel

Received May 24, 1966

The acetone- and benzophenone-initiated photochemical amidation of α,β-unsaturated esters with formamide is described. The reaction led to the corresponding alkylated succinic acid derivatives in yields of up to 90%. Ethyl cinnamate yielded 2-carbamoyl-3,4,4-triphenyl-γ-butyrolactone (when benzophenone was used as a photosensitizer), whereas addition of formamide to benzal diethyl malonate led to ethyl 2-ethoxycarbonyl-3-carbamoylhydrocinnamate. It was found that in the present case (i) the α,β-unsaturated ester and (ii) formamide compete for the excited (triplet) carbonyl compound: the reaction with i leads to *cis–trans* isomerization of the unsaturated ester and involves a genuine energy-transfer step; whereas the reaction with ii leads to addition of formamide to the double bond and involves a hydrogen atom abstraction step from formamide.

The light-induced addition of formamide to isolated double bonds (terminal, nonterminal, and cyclic) has been reported by us in previous papers of this series.[3] It was shown that this reaction could be induced directly by light or initiated photochemically by acetone with higher yields. The direct light-induced addition of formamide to ethyl maleate and fumarate has been reported by us in a preliminary communication.[4] We have found since then that this addition reaction of formamide to α,β-unsaturated esters could be initiated photochemically by ketonic photosensitizers, and the present paper gives full details of the reactions and the products obtained, using (mainly) benzophenone as a photosensitizer.[5]

Results

Formamide has been found to undergo acetone and benzophenone-initiated photochemical addition to aliphatic α,β-unsaturated esters to yield the derivatives of the corresponding alkylated succinic acids (Scheme I). The reaction product in the case of ethyl cinnamate, while using benzophenone as a sensitizer, was 2-carbamoyl-3,4,4-triphenyl-γ-butyrolactone, whereas benzal diethyl malonate gave ethyl 2-ethoxycarbonyl-3-carbamoylhydrocinnamate. The reactions studied and the major products obtained are summarized in Table I.

Products were isolated by standard procedures and identified by means of their physical properties and elemental analyses as well as by spectroscopic data. They were further hydrolyzed to the corresponding alkylated succinic acids, which were compared with authentic samples. 2-Carbamoyl-3,4,4-triphenyl-γ-butyrolactone was hydrolyzed to the corresponding acid which was then decarboxylated to yield 3,4,4-triphenyl-γ-butyrolactone. Ethyl 2-ethoxycarbonyl-3-carbamoylhydrocinnamate was hydrolyzed and decarboxylated to yield phenylsuccinic acid which was compared with an authentic sample. Products resulting from reactions between the benzophenone moiety and formamide were also isolated in most cases, though in poor yields. The major product of these reactions was the amide of benzilic acid.

TABLE I

ADDITION PRODUCTS OF FORMAMIDE AND α,β-UNSATURATED ESTERS[a] (INITIATED BY BENZOPHENONE)

Ester	Product (1:1 adduct)	%	Source of light
Ethyl maleate	Diethyl carbamoylsuccinate	90[b]	Sun
		82	Ultraviolet[c]
Ethyl fumarate	Diethyl carbamoylsuccinate	86	Ultraviolet[c]
Methyl 2-octenoate	Methyl 3-carbamoyloctanoate	80	Sun
		81	Ultraviolet[c]
Methyl 2-nonenoate	Methyl 3-carbamoylnonanoate	79	Ultraviolet[c]
Methyl 2-decenoate	Methyl 3-carbamoyldecanoate	93	Sun
		77	Ultraviolet[c]
Ethyl cinnamate	2-Carbamoyl-3,4,4-triphenyl-γ-butyrolactone	17	Sun
		21	Ultraviolet[c]
Benzal diethyl malonate	Ethyl 2-ethoxycarbonyl-3-carbamoylhydrocinnamate	40	Ultraviolet[c]

[a] Mole ratio of formamide/α,β-unsaturated ester was 1:250. [b] Yields are based on the ester employed. [c] Hanau Q 81 high-pressure mercury vapor lamps were used as radiation sources for these reactions.

Discussion

The mechanism of the addition reaction of formamide to olefins was discussed in our previous publications[3] and was shown to be a free-radical chain reaction involving carbamoyl·$CONH_2$ radicals. As

(1) Part III: D. Elad and J. Rokach, *J. Org. Chem.*, **30**, 3361 (1965).

(2) In partial fulfillment of the requirements for a Ph.D. degree submitted to the Feinberg Graduate School of The Weizmann Institute of Science.

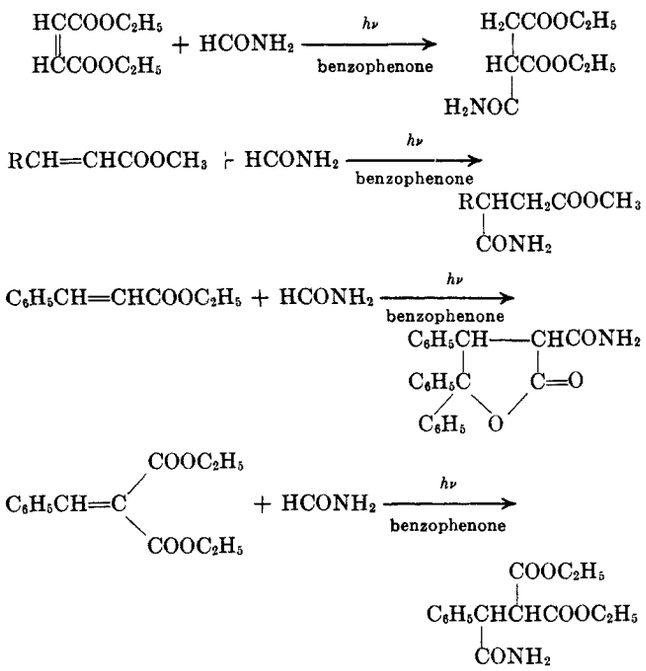
(3) (a) D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964); (b) D. Elad and J. Rokach, *J. Chem. Soc.*, 800 (1965); (c) D. Elad and J. Rokach, *J. Org. Chem.*, **30**, 3361 (1965).

(4) D. Elad, *Proc. Chem. Soc.*, 225 (1962).

(5) According to the mechanism proposed for the interaction of the photoactivated benzophenone molecule with formamide in the addition of the latter to isolated olefins,[3a] the ketonic compound should be termed a "photoinitiator" rather than a "photosensitizer." However, interaction of the excited carbonyl compound and the α,β-unsaturated esters in the present case (*vide infra*) is a genuine energy-transfer step and thus the ketonic compound acts here as a photosensitizer.[6]

(6) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshow, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964), and references cited therein.

SCHEME I[a]



[a] R = C_5H_{11}, C_6H_{13}, and C_7H_{15}.

far as the initiation step of this reaction is concerned, experimental data showed that the generation of carbamoyl radicals in solution was accomplished through hydrogen atom abstraction from formamide by the photoactivated acetone molecule. We concluded that the generation of the carbamoyl radicals from formamide through the photoexcitation of acetone involved a hydrogen atom abstraction step for the following reasons:[3a] (a) 2-methylalkan-2-ols were isolated from reaction mixtures of formamide and terminal olefins in the presence of acetone; (b) isopropyl alcohol was formed in photolyzed formamide–acetone mixtures,[7] and (c) considerable amounts of benzpinacol were formed when benzophenone was used as a photoinitiator. These experimental facts indicate that a ketyl species of the type $\begin{matrix}R\\R\end{matrix}\!\!>\!\!COH$ is formed in the reaction mixture; it is probably formed during the hydrogen atom abstraction step.

The possible interaction of the excited ketonic compound with isolated double bonds has been mentioned in our previous papers.[3c] This process is competitive with the interaction of the excited ketone with formamide and may serve as a quenching step. Energy-transfer processes from excited carbonyl compounds to isolated double bonds have been reported in the literature,[8] however, they do not seem to be very efficient, most probably because of the "high" triplet energy of the olefinic compound.[9] In the case of α,β-unsaturated esters the energy-transfer process from the excited carbonyl compound to the substrate has been reported to be efficient and led to chemical reactions, *e.g.*, *cis–trans* isomerization or cycloaddition.[6] The interaction of the photoactivated carbonyl compound with the olefinic system through energy transfer leads to quenching of the former and we are faced with a case in which this process is efficient and has, perhaps, to be taken into account while considering the initiation step of the formamide addition reactions. Thus, when the acetone-initiated reaction of formamide with ethyl maleate or fumarate was carried out under conditions similar to the ones used for isolated double bonds (*i.e.*, if a limited amount of acetone was employed), no addition products of formamide and the unsaturated ester could be detected. However, the recovered starting α,β-unsaturated ester consisted of a mixture of the two geometrical isomers (particularly in the case of ethyl fumarate when most of it was transformed into the maleate). This indicated that interaction between the excited sensitizer and the olefinic compound took place. Increase of the amount of acetone in the reaction mixture resulted in some addition of formamide to either ethyl maleate or fumarate; however yields of the formamide–ester adduct were still poor. This was probably due to chemical reactions between acetone and the α,β-unsaturated ester which took place when larger amounts of acetone were employed.[3a] As in previous experiments, the recovered ester consisted of a mixture of the two geometrical isomers, *i.e.*, maleate and fumarate. On the other hand, benzophenone was found as a suitable sensitizer for the addition reaction of formamide and α,β-unsaturated esters. The excited benzophenone molecules perform the undesirable energy-transfer step to the α,β-unsaturated ester, which is unavoidable under the reaction conditions, however, the hydrogen atom abstraction process from formamide also took place without any complications.[10] Thus, through the use of benzophenone we were able to effect the addition of formamide to both ethyl maleate and fumarate in almost quantitative yields (based on the α,β-unsaturated ester employed). The photoaddition of formamide to other α,β-unsaturated esters also took place in high yields when benzophenone was used as a sensitizer. Benzpinacol was formed in all cases. It seems from our experiments that the energy-transfer step to the α,β-unsaturated ester is more efficient and more rapid than the hydrogen atom abstraction step from formamide. By working up partially reacted reaction mixtures it has been noticed that *cis–trans* isomerization was faster than formation of benzpinacol and also faster than the formation of the addition product of formamide and the α,β-unsaturated ester. These experiments with ethyl maleate or fumarate are summarized in Tables II and III.

In Table II the generation of the two geometrical isomers of the α,β-unsaturated ester in solution, the formation of the addition product, as well as the formation of benzpinacol are described. As shown, *cis–trans* isomerization and formation of the addition product preceded the formation of benzpinacol. The formation of the 1:1 adduct and benzpinacol is faster in the

(7) H. Grossmann, *Z. Naturforsch.*, **20b**, 209 (1965).

(8) (a) A. C. Testa, *J. Org. Chem.*, **29**, 2461 (1964); (b) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); (c) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 5569 (1965).

(9) *Cf.* D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(10) It should be noted that photosensitizers having a low triplet energy and which might fail to perform the undesired *cis–trans* isomerization process of the α,β-unsaturated esters are not always suitable for the present cases, since they are not necessarily hydrogen abstraction agents in their excited state. This is due to the fact that their low-lying triplet state is not of the $n \rightarrow \pi^*$ nature. *Cf.* G. Porter and P. Suppan [*Trans. Faraday Soc.*, **61**, 1664 (1965)] and A. Schönberg ["Präparative Organische Photochemie," Springer-Verlag, Heidelberg, 1958, pp 111, 112].

TABLE II

ADDITION REACTION OF FORMAMIDE AND ETHYL FUMARATE (INITIATED BY BENZOPHENONE[a])

Time, min	Benzpinacol, g	Product (1:1 adduct), g	Maleate, %[b]
5	...	0.028	1.5
10	...	0.110	10
20	0.010	0.195	21
50[c]	0.025	0.600	42
80	0.180	1.3	69
135	0.450	2.4	92
280	2.3	3.25	98

[a] Employing 0.055 mole (10 g) of benzophenone, 0.017 mole (3 g) of ethyl fumarate, and 5 moles (225 g) of formamide (see Experimental Section). [b] In unreacted starting material. [c] It should be noted that while employing 0.028 mole of benzophenone under similar reaction conditions, 500 mg of 1:1 addition product was obtained after 50 min, while no benzpinacol could be detected.

TABLE III

ADDITION REACTION OF FORMAMIDE AND ETHYL MALEATE[a] (INITIATED BY BENZOPHENONE)

Time, min	Benzpinacol, g	Product (1:1 adduct), g
10	0.010	0.216
50[b]	0.110	1.1
80	0.400	2.0

[a] In these experiments the whole amount of maleate (or fumarate) was introduced into the reaction mixture at the beginning (see Experimental Section). [b] Employing 0.055 mole of benzophenone (see Table II). With 0.028 mole of benzophenone only 29 mg of benzpinacol could be isolated after 50 min, while 1.31 g of 1:1 addition product was formed during this period.

case of the maleate than in the case of fumarate, as can be seen by comparing Tables II and III. It is noteworthy that after short irradiation periods an addition product of formamide and the α,β-unsaturated ester is obtained (as well as *cis–trans* isomerization of the α,β-unsaturated ester), whereas no benzpinacol is detected. This observation seems surprising at first sight since one would assume that benzpinacol should accompany the formation of the adduct of formamide and α,β-unsaturated ester. It was noted too (see Tables II and III footnotes *b* and *c*, respectively) that at certain concentrations of benzophenone a considerable amount of the 1:1 addition product was obtained without any detectable formation of benzpinacol.

Since the addition reaction was carried out with light of wavelengths >300 mμ (Pyrex filter) it seems probable that the initiation step does not involve direct excitation of maleate (or fumarate) or formamide and that the ketonic sensitizer serves as the light-absorbing system. As previously shown, the initiation step of the reaction of formamide with olefins involves a hydrogen atom abstraction from formamide by the excited carbonyl compound,[3] and, thus the mechanism of the addition reaction of formamide to either maleate or fumarate can be pictured as follows.

$$(C_6H_5)_2C{=}O \xrightarrow{h\nu} (C_6H_5)_2C{=}O^z \quad (1)$$

$$(C_6H_5)_2C{=}O^z + HCONH_2 \longrightarrow (C_6H_5)_2\dot{C}OH + \cdot CONH_2 \quad (2)$$

$$\cdot CONH_2 + HC(CONH_2)(COOC_2H_5){=}CHCOOC_2H_5 \longrightarrow HC(CONH_2)(COOC_2H_5)CH(COOC_2H_5)\dot{C}H \quad (3)$$

$$HC(CONH_2)(COOC_2H_5)\dot{C}H + HCONH_2 \longrightarrow HC(CONH_2)(COOC_2H_5)CH_2CONH_2 + \cdot CONH_2 \quad (4)$$

$$2(C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2C(OH)C(OH)(C_6H_5)_2 \quad (5)$$

The absence of benzpinacol in the early stage of the photoreaction (Tables II and III) might indicate that steps 2 and 5 do not take place, but that the benzophenone is regenerated by genuine energy transfer to formamide, which then adds to the double bond. However, the following alternative should be considered.

$$HC(CONH_2)(COOC_2H_5)\dot{C}H + (C_6H_5)_2\dot{C}OH \longrightarrow HC(CONH_2)(COOC_2H_5)CH_2COOC_2H_5 + (C_6H_5)_2C{=}O$$

A similar observation was made by Pitts, *et al.*,[11] and by Schenck and co-workers[12] in the case of the benzophenone-photosensitized addition of isopropyl alcohol to maleic acid, where under certain reaction conditions terebinic acid (the 1:1 adduct) was isolated while no benzpinacol could be detected. This point needs further clarification as far as the mechanism involved in the regeneration of benzophenone is concerned. The interpretation of the experimental results is complicated by the possible difference in the rate of addition of the carbamoyl radical and the kinetic chain length of the reaction for both geometrical isomers, as well as by the mechanism of the regeneration of the benzophenone in this process. These points are now under investigation.

We have so far discussed the photochemical aspects of the addition of formamide to α,β-unsaturated esters. As noted previously,[3] this reaction is regarded as a free-radical chain reaction involving carbamoyl radicals $\cdot CONH_2$ and an olefin which serves as a scavenger for these radicals (reaction 6)

$$RCH{=}CH_2 + \cdot CONH_2 \longrightarrow R\dot{C}HCH_2CONH_2 \quad (6)$$

$$R\dot{C}HCH_2CONH_2 + HCONH_2 \longrightarrow RCH_2CH_2CONH_2 + \cdot CONH_2 \quad (7)$$

The chain-transfer step in which a new carbamoyl radical is produced through hydrogen atom abstraction from formamide is described in reaction 7. In order to obtain high yields of the 1:1 addition products it is necessary that reactions 6 and 7 be fast in comparison with all chain termination steps.[13,14] As for the orientation of addition of the carbamoyl radical to nonterminal olefins, it has been shown that the radical adds to either carbon atoms of the double bond, leading to a mixture of the two possible isomeric amides as the major products of the reaction. The relative

(11) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martine, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

(12) G. O. Schenck and co-workers, through personal communication from Dr. R. Steinmetz.

(13) C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963).

(14) J. I. G. Cadogen, *Roy. Inst. Chem. London, Lectures, Monographs, Rept.*, No. 6 (1961).

stability of the radicals formed and steric factors were given as reasons for the formation of both products.[3a] In the case of α,β-unsaturated esters of the type $R\overset{\beta}{C}H{=}\overset{\alpha}{C}HCOOR_1$ (R = alkyl) the initial attack of the carbamoyl radical is at the β carbon resulting in the formation of a free radical which obtains its stabilization through resonance with the ester group

$$RCH{=}CHCOOR_1 + \cdot CONH_2 \longrightarrow RC\dot{H}CHCOOR_1 \quad (CONH_2)$$

Experimental data showed that the amido esters resulting from such a radical were the only isomers formed (*i.e.*, derivatives of alkylated succinic acids) in reactions when R was a straight-chain alkyl group. Ethyl cinnamate presented an interesting case since "competition" between the relative stabilities of the

$$C_6H_5\dot{C}H(CONH_2)CH(COOC_2H_5) \quad \text{and} \quad C_6H_5CH(\dot{C}HCOOC_2H_5)(CONH_2)$$

two possible intermediate radicals can play a role in the orientation of the addition of the carbamoyl radical to this compound. Huang[15] compared the stability of free radicals which are stabilized by conjugation with a variety of functional groups and proposed the following stabilization series, $C_6H_5 > CN > COOEt > Me$. Thus, the addition of the carbamoyl radical to ethyl cinnamate should lead to $C_6H_5\dot{C}H{-}CH(CONH_2)(COOC_2H_5)$ as an intermediate radical which should subsequently yield a benzyl malonic acid derivative. However, experimental data show that the major product of addition of formamide to ethyl cinnamate sensitized by benzophenone is 2-carbamoyl-3,4,4-triphenyl-γ-butyrolactone. The formation of this product can be seen in Scheme II. This means that

SCHEME II

$$C_6H_5CH{=}CHCOOC_2H_5 + HCONH_2 \xrightarrow{h\nu} \xrightarrow{(C_6H_5)_2C{=}O}$$

$$[C_6H_5\dot{C}HCH(CONH_2)(COOC_2H_5)] \xrightarrow{(C_6H_5)_2\dot{C}OH}$$

I

$$C_6H_5CH(CONH_2)C(C_6H_5)(COOC_2H_5)(OH) \longrightarrow C_6H_5CH{-}C(CONH_2)(C_6H_5)C(=O)O$$

II III

the stable intermediate benzylic radical I in which the unpaired electron is delocalized over the phenyl group, fails to perform the hydrogen atom abstraction from formamide. Instead, it tends to combine with a semipinacol radical (or a benzophenone molecule), thus leading to the amido ester alcohol II which subsequently lactonizes to the amido lactone III. Infrared and nmr spectra of the product supported the proposed structure (see Experimental Section). Further proof of the assigned structure was obtained through hydrolysis of the amide to the corresponding carboxylic acid, followed by decarboxylation to 3,4,4-triphenyl-γ-butyrolactone which was found identical with an authentic sample. Addition products resulting from the alternative orientation of addition of the carbamoyl radical to ethyl cinnamate could not be detected.

Benzal diethyl malonate showed a different behavior toward addition of formamide than ethyl cinnamate.[16] The product of the addition reaction of formamide and benzal diethyl malonate was shown to be $C_6H_5CH(-CONH_2)CH(COOC_2H_5)_2$ and resulted from a different orientation of addition of the carbamoyl radical to the double bond than in ethyl cinnamate. Thus, the radical $C_6H_5CH(-CONH_2)\dot{C}(COOC_2H_5)_2$ was formed as the primary addition species. Eliminating steric factors, it seems that this radical is more stable than the isomeric benzylic-type radical. However, this radical did not react with a semipinacol radical, but performed the usual chain-transfer step, *i.e.*, it abstracted a hydrogen atom from formamide.[17]

In our previous publications of this series we reported the addition of acetone (when used as an initiator) to the olefin.[3] In the present case, *i.e.*, when benzophenone was employed instead of acetone, we also noticed some addition of the sensitizer to the α,β-unsaturated ester. However, the addition product, which was shown to be 3-ethoxycarbonyl-4,4-diphenyl-γ-butyrolactone, was isolated in small quantities only and results probably from the reaction shown in Scheme III.

SCHEME III

$$HCCOOC_2H_5 \,\|\, HCCOOC_2H_5 + (C_6H_5)_2\dot{C}OH \longrightarrow$$

$$[(COOC_2H_5)CH(CH_2COOC_2H_5)C(C_6H_5)(OH)C_6H_5] \longrightarrow (COOC_2H_5)C(C_6H_5)(C_6H_5)OC(=O)$$

Experimental Section[18]

Experiments with ultraviolet light were conducted in an immersion apparatus using Hanau Q 81 high-pressure mercury vapor lamps, which were cooled internally with running water.[19] Pyrex filters were used for all experiments unless otherwise stated. Agitation was achieved by magnetic stirring. Nitrogen was bubbled through the reaction mixture for the first 15 min. Reactions in sunlight were performed in Pyrex flasks and mixtures were stirred by magnetic stirring.

Reagents.—Formamide, pure grade, was freshly distilled at 0.2 mm before use; absolute acetone was used; benzophenone was pure grade; *t*-butyl alcohol was distilled over sodium. The α,β-unsaturated esters were freshly distilled before use. Methyl 2-octenoate had bp 98–100° (25 mm); methyl 2-nonenoate had bp 116–118° (25 mm); methyl 2-decenoate had bp 130–132° (25 mm).

Typical experiments with ultraviolet light and sunlight are described under A. Other experiments were conducted under similar conditions unless otherwise stated.

(15) R. L. Huang, *J. Chem. Soc.*, 1342 (1957), and references cited therein.

(16) M. Julia, personal suggestion and communication.

(17) *Cf.* G. H. Williams, *Progr. Stereochem.*, **2**, 39.

(18) For general experimental details see, D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964). The infrared spectra were determined on a Perkin-Elmer 137 instrument. The nmr data were obtained on a Varian A-60 instrument in the specified solvents and tetramethylsilane (TMS) as internal standard. The positions of the peaks are given in τ values.

(19) *Cf.* G. O. Schenck, *Dechema Monograph.*, **24**, 105 (1955).

A. Ethyl Maleate and Formamide. 1. With Ultraviolet Light.—A mixture of ethyl maleate (0.5 g), formamide (240 ml), *t*-butyl alcohol (40 ml), and benzophenone (10 g) was irradiated for 30 min. A solution of ethyl maleate (2.5 g) in *t*-butyl alcohol (10 ml) was then added during 30 min. A precipitate of benzpinacol appeared after 30 min. Irradiation was continued for another 2 hr. Benzpinacol (1 g) was filtered off and the filtrate was treated with saturated aqueous sodium chloride solution and extracted with chloroform. Evaporation of the solvent left a residue (11.5 g) which was chromatographed on alumina (400 g). Petroleum ether (bp 60–80°) eluted unchanged benzophenone. Acetone–petroleum ether (1:49) eluted benzpinacol (680 mg). The same solvent mixture further eluted 3-ethoxycarbonyl-4,4-diphenyl-γ-butyrolactone (180 mg), mp 148–150° (ether); ν_{max}^{KBr} 1725 and 1777 cm^{-1}; nmr ($CDCl_3$), a triplet centered at τ 9.1 (3 H, CH_2CH_3), a multiplet centered at 7.2 (2 H, $OCOCH_2$), a multiplet centered at 6.0 (3 H, $CHCOOCH_2CH_3$), and a multiplet centered at 2.6 (10 H, aromatic protons).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 74.02; H, 5.80.

Acid hydrolysis of the product led to 4,4-diphenyl-γ-butyrolactone, mp and mmp 88–90°; lit.[20] mp 87–90°.

Elution with acetone–petroleum ether (3:7) yielded diethyl carbamoylsuccinate (3.13 g, 82% yield, based on ethyl maleate employed), mp 76–78° (ether), $\nu_{max}^{CHCl_3}$ 1697 and 1726 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO_5$: C, 49.76; H, 6.96; N, 6.45. Found: C, 49.77; H, 7.00; N, 6.46.

Alkaline hydrolysis of the product gave 1,1,2-ethanetricarboxylic acid, mp 159–160° dec, which was found to be identical with an authentic sample.[21]

Acetone–petroleum ether (4:6) eluted benzilic acid amide, mp 153–154° (ether). This amide was found to be identical with an authentic sample prepared according to Kao.[22] The amounts of benzilic acid amide obtained in the various experiments ranged from 0.1 to 1 g. Unidentified polar fractions were eluted with acetone–ethanol mixtures.

2. In Sunlight.—A mixture of ethyl maleate (0.5 g), formamide (240 ml), *t*-butyl alcohol (40 ml), and benzophenone (10 g) was exposed to direct sunlight for 2 hr. A solution of ethyl maleate (2.5 g) in *t*-butyl alcohol (10 ml) was then added during 6 hr. Benzpinacol started precipitating after 5 hr. The mixture was left in direct sunlight for 3 days. It was worked up according to the procedure described above leading to an oily residue (12 g) which was chromatographed on alumina (400 g) to yield benzophenone, benzpinacol (600 mg), and diethyl carbamoylsuccinate (3.4 g, 90% yield). Unidentified polar fractions were eluted with acetone–ethanol mixtures.

Ethyl Maleate, Formamide, and Acetone with Ultraviolet Light.—A mixture of ethyl maleate (300 mg), formamide (60 ml), and acetone (20 ml) was irradiated for 4 hr. A solution of ethyl maleate (1.2 g) in acetone (10 ml) was then added overnight, and irradiation was continued for another 20 hr. The residue (2 g) left after the usual work-up was chromatographed on alumina (100 g) to yield 200 mg of diethyl carbamoylsuccinate.

B. Ethyl Fumarate and Formamide with Ultraviolet Light.—A mixture of ethyl fumarate (0.5 g), formamide (220 ml), *t*-butyl alcohol (30 ml), and benzophenone (10 g) was irradiated for 20 min. A solution of ethyl fumarate (2.5 g) in *t*-butyl alcohol (10 ml) was then added during 30 min. Benzpinacol precipitated after 3 hr. Irradiation was continued for another 1.5 hr. Benzpinacol (1.6 g) was filtered off and the filtrate was worked up by the usual procedure. Chromatography of the residue as described above led to benzophenone, an additional crop of benzpinacol (700 mg), 3-ethoxycarbonyl-4,4-diphenyl-γ-butyrolactone (100 mg), diethyl carbamoylsuccinate (3.25 g, 86% yield), and benzilic acid amide (100 mg).

C. Methyl 2-Octenoate and Formamide. 1. With Ultraviolet Light.—A mixture of methyl 2-octenoate (1 g), formamide (230 ml), *t*-butyl alcohol (35 ml), and benzophenone (10 g) was irradiated for 30 min. A solution of methyl 2-octenoate (3 g) in *t*-butyl alcohol (10 ml) was then added during 1 hr. Irradiation was continued for another 4 hr. Benzpinacol (2.3 g) was filtered off and the residue (12.5 g) obtained by the usual work-up was chromatographed on alumina (400 g) to yield benzophenone, benzpinacol (710 mg), and methyl 3-carbamoyloctanoate (4.18 g, 81% yield), mp 56–58° (ether–pentane), which was eluted with acetone–petroleum ether (3:7); ν_{max}^{KBr} 1660 and 1727 cm^{-1}; nmr ($CDCl_3$), a triplet centered at τ 9.08 (3 H, CH_2CH_3), a broad singlet at 8.7 (10 H, CH_2), a multiplet centered at 7.37 (3 H, $CH(CONH_2)CH_2COOCH_3$), a singlet at 6.3 (3 H, OCH_3), and a broad band at 4.1 (2 H, NH_2).

Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.67; H, 9.52; N, 6.96. Found: C, 60.03; H, 9.50; N, 7.19.

Alkaline hydrolysis of the product gave *n*-pentylsuccinic acid which was identical with an authentic sample.[23]

2. In Sunlight.—A mixture of methyl 2-octenoate (1 g), formamide (230 ml), benzophenone (10 g), and *t*-butyl alcohol (30 ml) was exposed to sunlight for 1 day. A solution of methyl 2-octenoate (3 g) in *t*-butyl alcohol (10 ml) was then added during 2 hr. The mixture was left in direct sunlight for 3 days. The usual work-up gave 2.5 g of benzpinacol. Chromatography of the residue which was left after the usual work-up yielded benzophenone, and additional crop of benzpinacol (600 mg) and methyl 3-carbamoyloctanoate (4.14 g, 80% yield).

D. Methyl 2-Nonenoate and Formamide with Ultraviolet Light.—The procedure described under C was followed using 4 g of methyl 2-nonenoate. The usual work-up led to 2.1 g of benzpinacol. Chromatography of the residue gave benzophenone, benzpinacol (800 mg), and methyl 3-carbamoylnonanoate (4 g, 79% yield), mp 64–66° (ether), ν_{max}^{KBr} 1660 and 1727 cm^{-1}.

Anal. Calcd for $C_{11}H_{21}NO_3$: C, 61.36; H, 9.83; N, 6.51. Found: C, 61.49; H, 9.71; N, 6.47.

The product yielded *n*-hexylsuccinic acid upon alkaline hydrolysis which exhibited mp and mmp 78–80°.[23]

E. Methyl 2-Decenoate and Formamide. 1. With Ultraviolet Light.—The procedure described under C was followed using 3 g of methyl 2-decenoate. The usual method of work-up led to 1.8 g of benzpinacol. Chromatography yielded benzophenone, benzpinacol (700 mg), and methyl 3-carbamoyldecanoate (2.9 g, 77% yield), which was eluted with acetone–petroleum ether (3:7) as an oil which crystallized upon standing and showed mp 72–74° (acetone–petroleum ether), ν_{max}^{KBr} 1660 and 1727 cm^{-1}.

Anal. Calcd for $C_{12}H_{23}NO_3$: C, 62.85; H, 10.11; N, 6.11. Found: C, 63.08; H, 10.06; N, 6.29.

Alkaline hydrolysis of the product led to *n*-heptylsuccinic acid which was found identical with an authentic sample.[23]

2. In Sunlight.—The procedure described under C in sunlight was followed using 3 g of methyl 2-decenoate. The mixture was worked up in the usual manner leading to 2.4 g of benzpinacol. Chromatography gave benzophenone, benzpinacol (1 g), and methyl 3-carbamoyldecanoate (3.5 g, 93% yield). Various amounts of benzilic acid amide could be isolated from different batches.

F. Ethyl Cinnamate and Formamide. 1. With Ultraviolet Light.—A mixture of ethyl cinnamate (2 g), formamide (240 ml), *t*-butyl alcohol (50 ml), and benzophenone (10 g) was irradiated for 6.5 hr. (Benzpinacol precipitates after 4.5 hr.) Benzpinacol (1.27 g) was filtered off and the mixture was worked up in the usual manner to yield benzophenone as well as an additional crop of benzpinacol (800 mg). Acetone–petroleum ether (3:7) eluted 2-carbamoyl-3,4,4-triphenyl-γ-butyrolactone (820 mg, 21% yield) which exhibited mp 214–216° after being treated with ether; ν_{max}^{KBr} 1690 and 1775 cm^{-1}; nmr (CD_3COCD_3), doublets centered at τ 6.83 (1 H, J = 12 cps) and 5.9 (1 H, J = 12 cps), and a multiplet centered at 3.7 (17 H, aromatic and NH_2 protons).

Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.24; H, 5.35; N, 3.97.

Alkaline hydrolysis of the amido lactone gave the acid lactone, which was decarboxylated at 180° to give 3,4,4-triphenyl-γ-butyrolactone, mp 159–160° (ether), lit.[24] mp 160–161°. The compound was found identical with an authentic sample prepared according to Scholtis.[24]

2. In Sunlight.—The same quantities used for the former experiment were employed exposing the reaction mixture to direct sunlight for 2 days. The usual work-up led to 700 mg (17%) of 2-carbamoyl-3,4,4-triphenyl-γ-butyrolactone.

G. Benzal Diethyl Malonate and Formamide with Ultraviolet Light.—A mixture of benzal diethyl malonate (3 g), formamide (240 ml), benzophenone (10 g), and *t*-butyl alcohol (50 ml) was irradiated for 5 hr. (Benzpinacol precipitated after 4 hr). Benzpinacol (1.3 g) was filtered off and the filtrate was worked up in the usual way leading to benzophenone and an additional

(20) W. S. Johnson, Jack W. Petersen, and W. P. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).

(21) F. W. Kay and W. H. Perkin, *J. Chem. Soc.*, **89**, 1640 (1906).

(22) C. H. Kao and Shao-Yuan Ma, *ibid.*, 443 (1931).

(23) K. Bernhard and H. Lincke, *Helv. Chim. Acta*, **29**, 1457 (1946).

(24) K. Scholtis, *Ann.*, **557**, 82 (1947).

crop of benzpinacol (750 mg). Acetone–petroleum ether (1:4) eluted an oil (1.5 g) believed to be a dimeric product of the unsaturated ester. Ethyl 2-ethoxycarbonyl-3-carbamoylhydrocinnamate (1.43 g, 40% yield), mp 119–121° (acetone–petroleum ether) was eluted with acetone–petroleum ether (1:3) and isolated from the oily fraction by crystallization, ν_{max}^{KBr} 1680 and 1718 cm^{-1}; nmr ($CDCl_3$), two triplets centered at τ 9.1 (3 H, J = 7 cps; CH_2CH_3) and 8.7 (3 H, J = 7 cps, CH_2CH_3), two quartets centered at 6.1 (2 H, J = 7 cps, CH_2CH_3) and 5.8 (2 H, J = 7 cps, CH_2CH_3) on which a singlet is superimposed at 5.75 (2 H), a broad band at 4.0 (2 H, NH_2), and a band at 2.6 (5 H, aromatic protons).

Anal. Calcd for $C_{15}H_{19}NO_5$; C, 61.42; H, 6.53; N, 4.78. Found: C, 61.70; H, 6.51, N, 4.72.

Alkaline hydrolysis of the amido diester led to the tricarboxylic acid which was decarboxylated at 190–200° to give phenyl succinic acid, mp and mmp 165–167°, lit.[25] mp 164–166°.

Acetone–petroleum ether (3:7) finally eluted benzilic acid amide (300 mg), mp 150–152°.

H. Ethyl Maleate and Formamide without Benzophenone.—A mixture of ethyl maleate (8 g) and formamide (110 g) was irradiated for 45 hr. (A quartz filter was used for this experiment.) The usual work-up led to 1.3 g (25%) of diethyl carbamoylsuccinate.

Similar results were obtained when ethyl fumarate was employed.

Acknowledgment.—We are indebted to the Feinberg Graduate School at the Weizmann Institute of Science for maintenance of a fellowship to one of us (J. R.).

(25) A. Lapworth and W. Baker, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p 451.

The Structures and Spectral Properties of Enamines and Iminium Salts of 1-Azabicycloalkanes

MANFRED G. REINECKE[1a] AND LOUIS R. KRAY[1b]

Departments of Chemistry, University of California, Riverside, California, and Texas Christian University, Fort Worth, Texas 76129

Received May 31, 1966

The infrared and nuclear magnetic resonance spectra of several enamines of 1-azabicycloalkanes and their corresponding iminium salts have been determined and interpreted to afford the following conclusions. (i) The position of the double bond in the enamines appears to be controlled by the same factors which are responsible for the relative stability of simple olefins and not those which are important for many enamines of cyclic ketones. (ii) The nmr spectra of the iminium salts contain characteristic, well-resolved peaks which are quite useful for structure determinations. (iii) The diagnostic generalization that converting an enamine to its salt results in a shift of the 6-μ infrared peak to higher frequencies is subject to exceptions.

The structures of enamines of unsymmetrical ketones and iminium salts are of theoretical and synthetic significance. For example, the preferential formation, in certain cases, of the less substituted enamines of cyclic ketones[2-7] has been rationalized by stereochemical arguments[2,8-11] which have proven to be of value in the conformational analysis of other systems.[12] From the synthetic point of view, the structures of the products obtained by electrophilic substitutions on the β carbon atoms of enamines have been assumed,[2,13,14] by analogy with the isoelectronic enolate ion,[15] to reflect the location of the double bond in the starting enamine.

One class of enamines whose structures have not been thoroughly investigated is that prepared[16] from the readily available[17] 1-azabicycloalkanes. In conjunction with another study[14] the infrared and nuclear magnetic resonance spectra of several such enamines and their iminium salts have been obtained and structural correlations have been established.

Results and Discussion

The enamines in Table I were prepared by the mercuric acetate oxidation[16,17] of the corresponding 1-azabicycloalkanes, the synthesis of all but two of which were reported previously from this laboratory.[17] Although one of these two, 1-ethylindolizidine (**4a**), was prepared in high yield by the Raney nickel catalyzed cyclization method[17] (**1** → **2** → **3** → **4**), the phenyl-substituted piperidyl alcohol **3b** (Scheme I) was converted to a diastereoisomeric mixture of 1-phenylindolizidenes (**4b**) to the extent of only 9% under identical conditions. The failure of the piperidyl alcohol **3b** to undergo normal cyclization apparently was due to poisoning of the catalyst since the Raney nickel recovered from the reaction mixture was no longer active in the cyclization of the piperidylalcohol **3** (R = H) to indolizidine[17] (**4**, R = H). 1-Phenylindolizidine (**4b**) was finally prepared in satisfactory yield by basification of the bromide–hydrobromide of the piperidyl alcohol **3b**.

The nmr spectra of these enamines (Table I) contain four general areas of proton absorption. The vinyl protons appear as broad singlets, or in one case (**9**) a poorly resolved triplet, at τ = 5.65–5.98 ppm. The abnormally high chemical shifts of these peaks[18] has

(1) (a) To whom inquiries should be sent at Texas Christian University; (b) National Science Foundation Summer Teaching Fellow, 1963; National Institute of Health Predoctoral Fellow in Chemistry, 1963–1965.

(2) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovikz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(3) M. E. Kuehne, *ibid.*, **81**, 5400 (1959).

(4) W. D. Gurowitz and M. A. Joseph, *Tetrahedron Letters*, 4433 (1965).

(5) S. K. Malhotra and F. Johnson, *ibid.*, 4027 (1965).

(6) G. Stork, XVIth National Organic Symposium Abstracts, Seattle, Wash., June 1959, p 44.

(7) G. Opitz and H. Mildenberger, *Ann.*, **650**, 115 (1961).

(8) W. R. N. Williamson, *Tetrahedron*, **3**, 314 (1958).

(9) H. J. Schaeffer and V. K. Jain, *J. Org. Chem.*, **29**, 2595 (1964).

(10) F. Johnson and A. Whitehead, *Tetrahedron Letters*, 3825 (1964).

(11) S. Danishefsky and M. Feldman, *ibid.*, 1131 (1965).

(12) F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5492 (1965).

(13) G. Bianchetti, D. Pocar, P. D. Croce, and A. Vigevani, *Chem. Ber.*, **98**, 2715 (1965).

(14) M. G. Reinecke and L. R. Kray, *J. Org. Chem.*, **30**, 3671 (1965).

(15) H. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 133.

(16) N. J. Leonard, A. S. Hay, R. W. Fulmer, and V. W. Gash, *J. Am. Chem. Soc.*, **77**, 439 (1955).

(17) M. G. Reinecke and L. R. Kray, *J. Org. Chem.*, **29**, 1736 (1964).

(18) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 61.