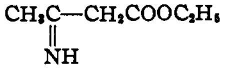
[Contribution from the Department of Chemistry, Columbia University]

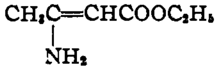
Structure of β-Amino Derivatives of α,β-Unsaturated Lactones and Esters

By Samuel A. Glickman and Arthur C. Cope

Ethyl β-aminocrotonate (I) and ethyl β-methylaminocrotonate (II) have been shown to exist in the enamine rather than the tautomeric imino forms by von Auwers and Susemihl.[1]

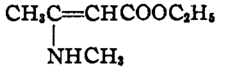


$CH_3\underset{\underset{NH}{\|}}{C}{-}CH_2COOC_2H_5$



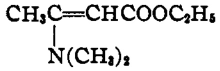
$CH_3\underset{\underset{NH_2}{|}}{C}{=}CHCOOC_2H_5$

I



$CH_3\underset{\underset{NHCH_3}{|}}{C}{=}CHCOOC_2H_5$

II

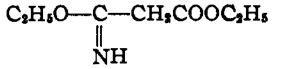


$CH_3\underset{\underset{N(CH_3)_2}{|}}{C}{=}CHCOOC_2H_5$

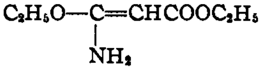
III

These esters and ethyl β-dialkylaminocrotonates, which can have only an α,β-unsaturated structure, were found to have approximately equal specific exaltations in refraction. Similar data support an enamine structure for β-amino-α,β-unsaturated nitriles and β-amino-α,β-unsaturated ketones.[1,2]

Imino derivatives related to the esters of 1,3-dicarboxylic acids also have structural features which permit imino–enamine tautomerism. For example, the imino compound related to ethyl malonate could exist as the enamine, V. Comparing the oxygen analogs of I and V, ethyl acetoacetate contains an appreciable percentage of the enol form, but ethyl malonate does not.



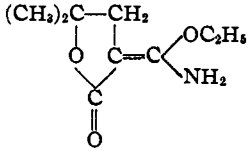
$C_2H_5O{-}\underset{\underset{NH}{\|}}{C}{-}CH_2COOC_2H_5$



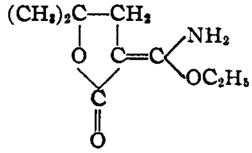
$C_2H_5O{-}\underset{\underset{NH_2}{|}}{C}{=}CHCOOC_2H_5$

V

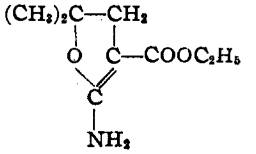
Consequently, structure V could not be predicted with certainty by analogy with I. It was therefore surprising to note that the compounds designated in the preceding paper as IV (formula C, D or E) and IX (formula C′, D′ or E′) have exaltations in refraction indicating that they are β-amino-α,β-unsaturated lactones or esters, rather than the isomeric imino compounds.[3] These structures are analogous to V, with the added complexities of alkyl substitution and a lactone ring.



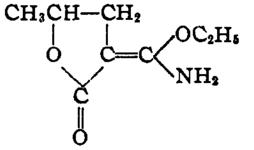
C



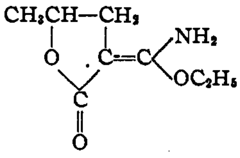
D



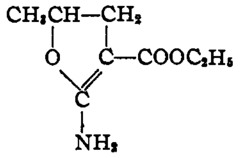
E



C′

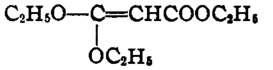


D′



E′

The compound with the structure of V or its tautomer was prepared by treating ethyl cyanoacetate with absolute alcohol and hydrogen chloride, and liberating the base from the resulting hydrochloride. It has an exaltation in refraction indicating that it is actually the enamine, V. The specific and molecular exaltations for these compounds and for ethyl β,β-diethoxyacrylate (VI) are listed in Table I.



$C_2H_5O{-}\underset{\underset{OC_2H_5}{|}}{C}{=}CHCOOC_2H_5$

VI

Table I

Compound	Exaltation in molecular refraction	Specific exaltation
I[a]	2.72	2.11
II[a]	2.79	1.95
III	3.39	2.16
IV	2.46	1.44
IX	2.69	1.45
V	1.80	1.13
VI	2.06	1.09

[a] Refraction data observed for I and II are in agreement with values reported in ref. 1.

Ultraviolet absorption spectra have been determined for all of these compounds, in order to obtain additional evidence concerning their structure. Imino forms related to structures I-IX are not conjugated, and would have absorption maxima at shorter wave lengths and lower log ε values than the conjugated enamine forms. Acetimino ethyl ester, $CH_3C(OC_2H_5){=}NH$, examined as a reference compound containing an imino-ester group, showed no absorption in cyclohexane solution in the region above 2200 Å.

Absorption spectra of the three β-aminocrotonic esters, I, II and III, in cyclohexane solution are shown in Fig. 1. All show intense absorption in the region of 2675 to 2825 Å., indicating the presence of conjugation and thus confirming the enamine structure of I and II. III serves as a model compound for this structure. The following maxima and log ε values were observed: I, $\lambda_{max.}$ 2675 Å. (log ε = 4.21); II, $\lambda_{max.}$ 2825 Å. (log ε = 4.25); III, $\lambda_{max.}$ 2750 Å. (log ε = 4.33).

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(1) von Auwers and Susemihl, *Ber.*, **63**, 1072 (1930).

(2) von Auwers and Wunderling, *ibid.*, **64**, 2748, 2758 (1931).

(3) Glickman and Cope, This Journal, **67**, 1012 (1945). Roman numerals IV, VII, IX and X are used to designate the same compounds in both papers.

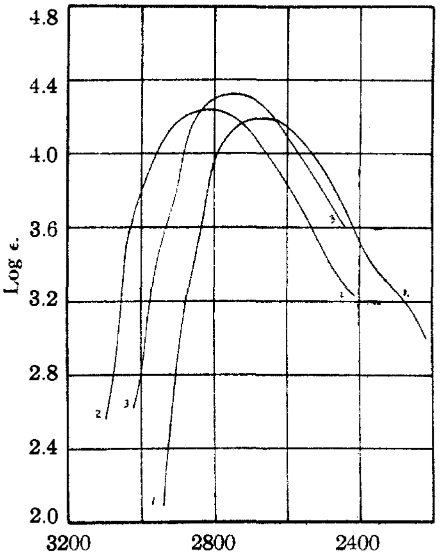

Fig. 1.—Curve 1, absorption spectrum of ethyl β-aminocrotonate; curve 2, ethyl β-methylaminocrotonate; curve 3, ethyl β-dimethylaminocrotonate. All determinations are in cyclohexane.

The absorption curves of I and III in alcohol are shifted to longer wave lengths and higher extinction coefficients (Fig. 2): I, $\lambda_{max.}$ 2740 Å. (log ε = 4.31)[4]; II, $\lambda_{max.}$ 2840 Å. (log ε = 4.51).

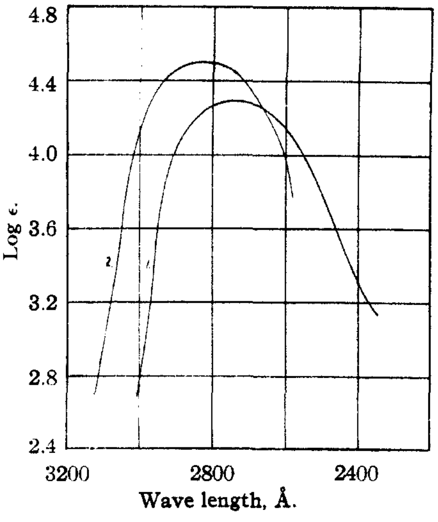

Fig. 2.—Curve 1, absorption spectrum of ethyl β-aminocrotonate; curve 2, ethyl β-dimethylaminocrotonate. Determinations are in absolute alcohol.

This shift is to be expected on changing from a non-polar to a polar solvent. The magnitude of the shift in wave length (65–90 Å.) is in agreement with the average difference of 70 Å. noted for the maxima of α,β-unsaturated carbonyl compounds in hexane and alcohol.[5]

The absorption spectra of V and VI in cyclohexane are shown in Fig. 3. The amino compound (V) absorbs at a longer wave length ($\lambda_{max.}$ 2540 Å. (log ε = 4.11)) than the corresponding ethoxy derivative (VI) ($\lambda_{max.}$ 2340 Å. (log ε = 4.16)). The maximum of V in alcohol (Fig. 4) is shifted to 2605 Å. (log ε = 4.24).

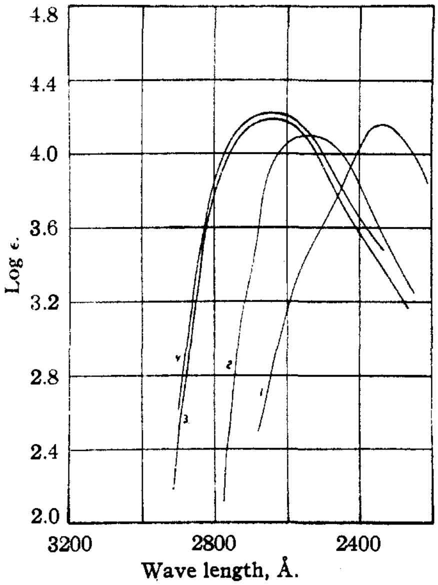

Fig. 3.—Curve 1, absorption spectrum of ethyl β,β-diethoxyacrylate; curve 2, ethyl β-amino-β-ethoxyacrylate; curve 3, compound IX; curve 4, compound IV. Determinations are in cyclohexane.

The absorption curves of IV (formula C, D or E) and IX (formula C′, D′ or E′) (Fig. 3) have maxima at 2660 Å. (log ε = 4.23) and 2645 Å. (log ε = 4.19), respectively, in cyclohexane solution. Intense absorption in this region indicates the presence of a conjugated system, and confirms the enamine structures assigned to IV and IX on the basis of their exaltation in refraction.

In the preceding paper a compound VII isomeric with IV was reported, which from its chemical properties must be either an imino form or an isomeric enamine. The absorption curve of this isomer (VII) in alcohol solution is shown in Fig. 5. Its maximum is at 2780 Å. (log ε = 4.33), compared to a maximum of 2720 Å. (log ε = 4.35) for IV in alcohol (Fig. 5). The intensity and wave length of the absorption of VII prove that it contains a conjugated system and therefore excludes imino forms as possible structures. IV and VII are consequently isomeric enamines, and correspond to two of the three structures C, D and E.

The presence of a conjugated system in X, isomeric with IX, was likewise demonstrated by

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(4) Baly and Desch, *J. Chem. Soc.*, **85**, 1039 (1904), report $\lambda_{max.}$ in alcohol *ca.* 2755 Å.; Brannigan, Macbeth and Stewart, *ibid.*, **103**, 414 (1913), give $\lambda_{max.}$ in alcohol *ca.* 2730 Å.

(5) Scheibe, Rössler and Backenköhler, *Ber.*, **58**, 586 (1925); Woodward, THIS JOURNAL, **63**, 1123 (1941).

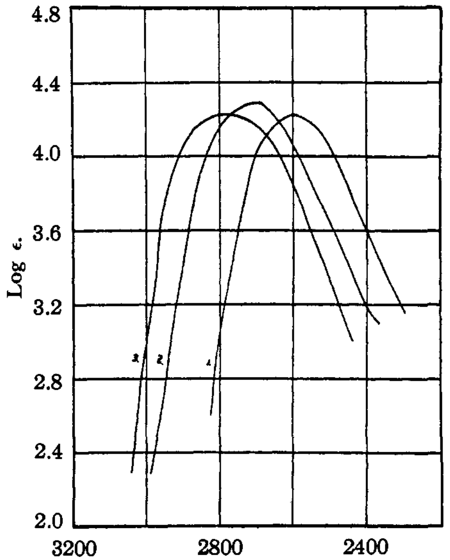

Fig. 4.—Curve 1, absorption spectrum of ethyl β-amino-β-ethoxyacrylate; curve 2, compound IX; curve 3, compound X. Determinations are in absolute alcohol.

means of its absorption curve. The $\lambda_{\text{max.}}$ for X in alcohol (Fig. 4) is at 2780 Å. (log ε = 4.25) and that for IX is at 2715 Å. (log ε = 4.29). Thus the enamines IX and X correspond to two of the structures C′, D′ and E′.

Experimental[6]

Ultraviolet Absorption Spectra.—The instrument was a Hilger medium quartz spectrograph equipped with a logarithmic rotating sector. The light source was a hydrogen discharge tube. In Figs. 1–5, the logarithms of the molar extinction coefficients are plotted against wave length in Ångström units. The compounds used in these determinations are described below or in the preceding paper.[3]

Ethyl β-Aminocrotonate (I).—A rapid stream of dry ammonia gas was passed through 97.5 g. of ethyl acetoacetate with stirring for five hours. The temperature rose to 40° during the first hour, and was kept at 35–40° by cooling. Ether (100 ml.) was added and the water which had formed was separated. The ether solution was distilled *in vacuo* through a Widmer column. The yield of I was 88.2 g. (90%), b. p. 91–93° (8–9 mm.); $n^{25}\mathrm{D}$ 1.4980; $d^{25}{}_4$ 1.0167; $M\mathrm{D}$ calcd. 34.52, found 37.24 (exaltation 2.72).[7]

Ethyl β-Methylaminocrotonate (II).[8]—The preparation was exactly similar to I, except that methylamine gas was passed through the ester for three hours. The yield of II was 97 g. (90%), b. p. 97° (9 mm.); $n^{25}\mathrm{D}$ 1.5017; $d^{25}{}_4$ 1.0006; $M\mathrm{D}$ calcd. 39.32, found 42.11 (exaltation 2.79).

Ethyl β-Dimethylaminocrotonate (III).[9]—The preparation was exactly similar to I, except that dimethylamine gas was used. II was obtained in 96.2 g. (82%) yield; b. p. 121–122° (9 mm.); $n^{25}\mathrm{D}$ 1.5188; $d^{25}{}_4$ 1.0006; $M\mathrm{D}$ calcd. 44.28, found 47.67 (exaltation 3.39).

Ethyl β-Amino-β-ethoxyacrylate (V).—Ethyl cyanoacetate (226 g., 2 moles), absolute alcohol (101 g., 2.2 moles) and dry ether (100 g.) were placed in a 1-liter filter flask and cooled in an ice–salt-bath. Dry hydrogen chloride was passed through the solution until the increase in weight was 83.5 g. The flask was stoppered and kept in an ice-bath for twenty-four hours. The hydrochloride, which crystallized as a hard mass of stout prisms, was broken up, filtered rapidly with suction, washed with dry ether and stored in a vacuum desiccator over calcium chloride; yield 299 g. (76%), m. p. 99–101° (dec.).

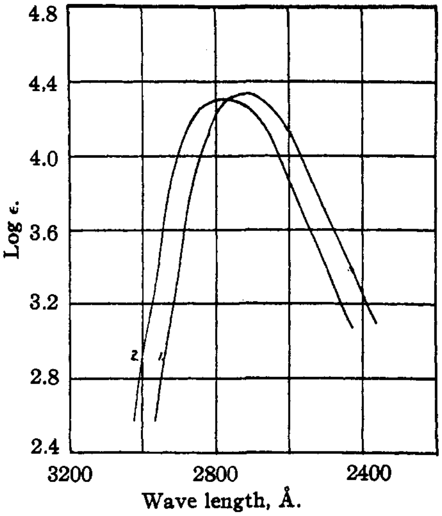

Fig. 5.—Curve 1, absorption spectrum of compound IV; curve 2, compound VII. Determinations are in alcohol.

The above hydrochloride (199 g.) was added slowly to an ice-cold mixture of 1 liter of water, 170 g. of sodium bicarbonate and 500 ml. of ether, with rapid stirring. The ether layer was separated and the aqueous layer was extracted with three 100-ml. portions of ether. The combined ether solutions were washed with a small amount of water, dried over sodium sulfate and concentrated. Distillation of the residue through a Widmer column yielded 152.2 g. (94%) of V, b. p. 96–99° (7–9 mm.); m. p. 35–36.5°. The supercooled liquid had $n^{25}\mathrm{D}$ 1.4810; $d^{25}{}_4$ 1.0606; $M\mathrm{D}$ calcd. 40.91, found 42.71 (exaltation 1.80).[10]

Anal. Calcd. for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.79. Found: C, 52.82; H, 8.46; N, 8.56.

Ethyl β,β-Diethoxyacrylate (Carbethoxyketene Acetal) (VI).—The above hydrochloride (100 g.) was allowed to stand with 200 g. of absolute alcohol in a stoppered flask at room temperature for two weeks. Dry ether (100 ml.) was added and the mixture was allowed to stand overnight in an ice-bath. The ammonium chloride was filtered and the filtrate distilled through a Widmer column in an atmosphere of nitrogen. Redistillation of the fraction b. p. 122–123° (10 mm.) yielded 31.0 g. (33%) of VI, b. p. 122° (9 mm.); $n^{25}\mathrm{D}$ 1.4597; $d^{25}{}_4$ 1.0242; $M\mathrm{D}$ calcd. 48.24, found 50.30 (exaltation 2.06).[11]

Acetimino Ethyl Ester.—Acetonitrile (82 g.) was converted into acetimino ethyl ester hydrochloride[12] by

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(6) Melting and boiling points are uncorrected.

(7) Michaelis, *Ann.*, **366**, 337 (1909), reports a similar preparation. Brühl, *Z. physik. Chem.*, **16**, 216 (1895), reports physical constants in agreement with these.

(8) Kuckert, *Ber.*, **18**, 618 (1885).

(9) Lauer and Jones, This Journal, **59**, 232 (1937).

(10) The hydrochloride has been prepared by: (a) Pinner, *Ber.*, **26**, 478 (1893); (b) Hessler, *Am. Chem. J.*, **22**, 169 (1899); (c) Reitter and Weindel, *Ber.*, **40**, 3359 (1907). Refs. 10a and 10b state that the free base is an oil, but do not report physical constants or analytical data. The compound was designated by the latter as carbethoxyacetimino ethyl ester and monoiminomalonic ester. (d) After this paper was prepared for publication, Weissberger, Porter and Gregory, This Journal, **66**, 1852 (1944), reported the preparation of "ethyl malonate monoimidoester," purified by recrystallization from petroleum ether, m. p. 42–43°. By their procedure, including recrystallization, we obtained a product with physical properties confirming those noted above; m. p. 35–37°; $n^{25}\mathrm{D}$ 1.4810; $d^{25}{}_4$ 1.0607 (supercooled liquid).

(11) Ref. 10c reports b. p.127.2–128.2° (12 mm.), d_{15} 1.0350.

(12) Pinner, *Ber.*, **16**, 1654 (1883).

the procedure described for I hydrochloride, except that the reaction mixture was allowed to stand for five days; yield 242 g. This hydrochloride (123.5 g.) was added slowly to an ice-cold mixture of 500 ml. of water, 276 g. of potassium carbonate and 200 ml. of ether, with rapid stirring. The aqueous layer was extracted once with 100 ml. of ether, and the combined ether solutions were dried over sodium sulfate and distilled through an adiabatic, total reflux, variable take-off type column with a 70 × 1.2 cm. section packed with glass helices. The yield of acetimino ethyl ester was 19.0 g. (22%), b. p. 89.7–90° (765 mm.); n^{25}_D 1.4025; d^{25}_4 0.8671; M_D calcd. 24.27, found 24.49.[13]

Summary

The ultraviolet absorption curve (in cyclohexane) of ethyl β-dimethylaminocrotonate (III) has a maximum at 2750 Å. ($\log \epsilon = 4.33$), corresponding to the absorption of the conjugated system present. Ethyl β-aminocrotonate (I) and ethyl β-methylaminocrotonate (II) absorb in the same region with similar intensity, confirming their structure as "enamines." Enamine structures have been assigned to these compounds by von Auwers and Susemihl on the basis of their exaltation in refraction.

Ultraviolet absorption and exaltation in refraction also prove that a conjugated system is present in ethyl β-amino-β-ethoxyacrylate, and accordingly the enamine structure V is assigned to this compound. V is a tautomer of monoiminomalonic ester. Its enamine structure is in contrast to the non-enolic structure of ethyl malonate.

Four compounds, either lactones or esters, related in structure to V (IV, VII, IX and X, ref. 3) have ultraviolet absorption spectra which show that they contain conjugated systems and consequently are enamines rather than isomeric imino compounds.

New York, N. Y. Received November 15, 1944

[13] Brühl, *Z. physik. Chem.*, **22**, 388 (1897); and Kohlrausch, *ibid.*, **B38**, 72 (1937), report similar physical constants.

[Contribution from the Richmond Laboratories, California Research Corporation]

Investigation of the Mechanism of Butane Isomerization Using Radioactive Hydrogen as a Tracer

By T. M. Powell[1] and E. B. Reid[2]

With increasing commercial importance of the isomerization of paraffin hydrocarbons, a knowledge of the mechanism of these reactions becomes of greater interest. Several mechanisms have been proposed but many have been without experimental foundation[3,4] and there have been few attempts to apply any specific function to the catalyst. The recent work of Heldman[5,6,7] is an independent work giving many of the conclusions obtained in this paper.

Utilizing the radioactive hydrogen isotope, H^3 (hereafter called tritium, abbreviated as T), as a tracer, an attempt has been made to determine the steps involved in the reaction, n-butane $\leftrightarrows$ isobutane, carried out over aluminum chloride on alumina and charcoal supports.

A number of investigations have been made using tritium as a tracer in chemical and hydrogen exchange reactions.[8-12] Advantage is taken in this case of the fact that during catalytic isomerization, an exchange of hydrogen atoms from both elementary hydrogen (H_2) and hydrogen chloride with the hydrogen atoms of butane occurs. The presence of hydrogen apparently does not alter the progress of the reaction, whereas hydrogen chloride is essential as shown by previous investigations.[13]

Materials.—The tritium used in these experiments was furnished through the courtesy of the Radiation Laboratory of the University of California, and was produced by deuteron–deuteron bombardment during operation of the sixty-inch cyclotron at Berkeley. It was obtained in the chemical form of water with a specific activity of 5.0×10^9 disintegrations per mole per minute.

The gaseous radioactive hydrogen was prepared by electrolyzing a dilute acid solution of this water in a glass cell fitted with platinum electrode separated by a sintered glass plate to prevent diffusion of the evolved gases.

The normal butane was removed from an industrial gas fraction by successive fractional distillation. The isobutane was prepared from isobutene (made by dehydrating tertiary butyl alcohol over alumina) by hydrogenation with electrolytic hydrogen over a copper catalyst prepared after the manner of Kistiakowsky, *et al.*[14] The normal butane and the isobutane used in the experiments were over 99% pure.

The radioactive hydrogen chloride was prepared by treating the electrolyzed radioactive hydrogen with elementary chlorine over an activated carbon catalyst at 300° and by dropping radioactive sulfuric acid (96%) on sodium chloride.

The butanes with the selectively placed tritium atoms were prepared by hydrolyzing the corresponding butyl magnesium bromides with acid solutions of radioactive

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[1] Present address: Standard Oil Company of California, San Francisco, Calif.

[2] Present address: Chemical Warfare Service, United States Army.

[3] Montgomery, McAteer and Franke "Catalytic Isomerization of Paraffin Hydrocarbons," Petroleum Division, A. C. S. Meeting, Preprint Baltimore Meeting, 1939.

[4] Egloff, Komarewsky and Hulla, "Hydrocarbons and Their Isomerization," same as above.

[5] Leighton and Heldman, This Journal, **65**, 2276 (1943).

[6] Heldman, *ibid.*, **66**, 1786 (1944).

[7] Heldman, *ibid.*, **66**, 1789 (1944).

[8] Allen and Ruben, *ibid.*, **64**, 948–950 (1942).

[9] Harman, Stewart and Ruben, *ibid.*, **64**, 2293–2294 (1942).

[10] Fontana, *ibid.*, **64**, 2503–2504 (1942).

[11] Norris, Ruben and Allen, *ibid.*, **64**, 3037 (1942).

[12] Harman, Stewart and Ruben, *ibid.*, **64**, 2294–2296 (1942).

[13] Glasebrook, Phillips and Lovell, *ibid.*, **58**, 1944 (1936).

[14] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 65–75 (1935).