TABLE I

REACTION OF 1-ALKOXY-1,3-ALKADIENES AND PARAFORMALDEHYDE

Dienes, Moles	Paraformaldehyde, Moles	Product 5,6-Dihydro-2*H*-pyran	Yield, %
1-Ethoxy-1,3-butadiene, 6.0[a]	6.0	2-Ethoxy, I	56
1-Methoxy-1,3-butadiene, 6.0[b]	6.0	2-Methoxy, II	62
1-(2-Methoxyethoxy)-1,3-butadiene, 1.5[b]	1.5	2-(2-Methoxyethoxy), III	30
1-(2-Ethylhexoxy)-1,3-butadiene, 0.18[b]	0.18	2-(2-Ethylhexoxy), IV	32
1-Methoxy-1,3-hexadiene, 4.4[c]	4.0	2-Methoxy-5-ethyl, V	21
1-Methoxy-2-ethyl-1,3-butadiene, 0.87[b]	0.92	2-Methoxy-3-ethyl, VI	29

[a] See the Experimental section for the general procedure which is described for this reactant combination. [b] This mixture was heated for 4 hours at 180° in an autoclave. DuPont "Antioxidant No. 5" (*p*-*N*-butylaminophenol in a mixed solvent of methanol and 2-propanol) was used as a polymerization inhibitor. [c] Pyrogallol (2 g.) was used as a polymerization inhibitor.

TABLE II

PROPERTIES AND ANALYSES OF PRODUCTS

			Carbon, %		Hydrogen, %		Unsaturation, %[a]		2,4-Dinitrophenylhydrazone[b]		
										Nitrogen, %	
Product	B.P., (mm.)	n^{20}_D	Calcd.	Found	Calcd.	Found	Calcd.	Found	M.P.	Calcd.	Found
I	53–54 (20)	1.4432	65.59	65.34	9.44	9.87	15.60	15.43	168–169.5[c]	20.00	19.88
II	59–60 (50)[d]	1.4452	63.13	63.10	8.84	9.20	17.50	17.25	168–169[c]	—	—
III	74–75 (5)	1.4531	60.74	60.90	8.92	9.00	12.64	12.62	165–167[c]	—	—
IV	93–94 (2)	1.4530	73.54	73.00	11.39	11.40	9.42	9.33	166–168[c]	—	—
V	69–70 (20)	1.4466	67.57	67.42	9.93	10.00	14.06	14.00	131–132	18.17	18.56
VI	67–69 (20)	1.4506	67.57	66.60	9.93	9.90	14.06	13.78	141–142	18.17	18.14

[a] Determined by bromination. [b] Prepared as described in the Experimental section. [c] Mixture melting point determinations showed no depression of melting points. [d] Other properties we have measured are: b.p. 136–138° (760 mm.); sp. gr. $^{20°}_{20°}$ 1.008; n^{25}_D 1.4425.

The 2,4-dinitrophenylhydrazone was made by adding the pyran to the standard reagent[9] and warming the mixture on a steam bath. The bright yellow plates (from ethanol-water) turned red at about 125° and then melted at 168–169.5° (analysis given in Table II).

The literature values for 2-ethoxy-5,6-dihydro-2*H*-pyran are[7]: b.p. 153–155°; n^{25}_D 1.4475; 2,4-dinitrophenylhydrazone, m.p. 159–160°. Because of the discrepancies of these values and of ours, we obtained an authentic sample of the pyran[10] and prepared the 2,4-dinitrophenylhydrazone under the same conditions we had used for our material. The derivative was identical to ours in appearance, melting point, and mixture melting point. Inasmuch as the 2,4-dinitrophenylhydrazone obtained by Woods and Sanders was prepared by hydrolyzing the pyran with aqueous acid to 5-hydroxy-2-pentenal and then adding the reagent, it is possible that the two materials are *cis-trans* isomers, ours being the *cis* and theirs the *trans*. To be sure that dehydration or other chemical changes had not occurred by the conversion of the yellow plates to the red plates we heated a sample at 142° in a drying pistol (under vacuum) for 3 hr.

Anal. Calcd. for $C_{11}H_{12}N_4O_5$: N, 20.00. Found: N, 19.75.

2-Ethoxytetrahydropyran. The 2-ethoxy-5,6-dihydro-2*H*-pyran (344 g., 2.68 moles) was hydrogenated over Raney nickel in a stirred autoclave. The 299 g. (86%) of 2-ethoxytetrahydropyran distilled at 46–47° (20 mm.); n^{20}_D 1.4247. The 2,4-dinitrophenylhydrazone melted at 106.5–107°. The corresponding values for an authentic sample of 2-ethoxytetrahydropyran[11] were: b.p. 46–47 (20 mm.), n^{20}_D 1.4250 and the 2,4-dinitrophenylhydrazone melted at 107–108°. The infrared spectra of the 2-ethoxytetrahydropyran from the two sources were identical.

2,4-Pentadienal. This material was prepared by the procedure essentially like that of Woods and Sanders.[7] A mixture of 128 g. (1.0 mole) of 2-ethoxy-5,6-dihydro-2*H*-pyran, 80 ml. of 85% phosphoric acid, and 200 ml. of water was stirred at room temperature for 30 min. The resulting homogeneous solution was steam distilled. The organic layer was dried and distilled to yield 20 g. (24%) of 2,4-pentadienal boiling at 37° (20 mm.); n^{20}_D 1.5173; and 2,4-dinitrophenylhydrazone of m.p. 173–174°. The reported values[7] for this material are: b.p. 37–38° (20 mm.); n^{20}_D 1.5163; and 2,4-dinitrophenylhydrazone of m.p. 176–177°.

DEVELOPMENT DEPARTMENT
UNION CARBIDE CHEMICALS CO.
DIVISION OF UNION CARBIDE CORP.
SOUTH CHARLESTON, W. VA.

---

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, 1956.

(10) We wish to thank Dr. G. F. Woods of the University of Maryland for this sample.

(11) Prepared as described by R. I. Longley, W. S. Emerson, and T. C. Shafer, *J. Am. Chem. Soc.*, **74**, 2012 (1952).

Two Stable α-Carbethoxy Ketenes[1]

MELVIN S. NEWMAN AND ERNEST A. ZUECH

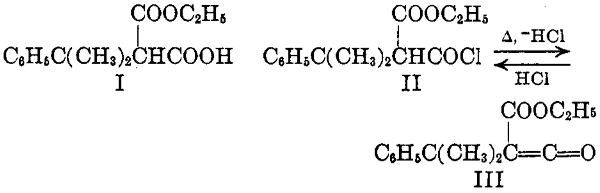
Received October 23, 1961

In the course of a synthetic scheme an attempt was made to convert α-carbethoxy-β-phenylisovaleric acid (I) to α-carbethoxy-β-phenylisovaleroyl chloride (II) by reaction with thionyl chloride.

---

(1) This research was supported by the Office of Ordnance Research, U. S. Army.

Subsequent distillation of the reaction products did not afford the desired acid chloride but (α,α-dimethylbenzyl)carbethoxyketene (III) in excellent yield.



$$\underset{\text{I}}{C_6H_5C(CH_3)_2\overset{\overset{\displaystyle COOC_2H_5}{|}}{C}HCOOH} \qquad \underset{\text{II}}{C_6H_5C(CH_3)_2\overset{\overset{\displaystyle COOC_2H_5}{|}}{C}HCOCl} \underset{HCl}{\overset{\Delta,\,-HCl}{\rightleftarrows}} \underset{\text{III}}{C_6H_5C(CH_3)_2\overset{\overset{\displaystyle COOC_2H_5}{|}}{C}=C=O}$$

It was later demonstrated that the acid chloride was formed and, upon heating, underwent a facile elimination of hydrogen chloride to give the ketene. To our knowledge this is the first example of ketene formation by pyrolysis of an acid chloride. This was found to be reversible as passage of anhydrous hydrogen chloride into the ketene readily gave the acid chloride. The structure of the ketene was substantiated by its preparation from the crude acid chloride by treatment with triethylamine.[2]

In addition to its ease of formation, (α,α-dimethylbenzyl)carbethoxyketene is noteworthy in that no dimerization was observed upon standing for six months at room temperature. This unusual stability was attributed to the bulkiness of the α,α-dimethylbenzyl grouping and not to any conjugation of the carbethoxy grouping, as ethylcarbethoxyketene[3] and phenylcarbethoxyketene[4] are known to undergo dimerization.

In support of the above premise, *tert*-butylcarbethoxyketene was prepared and similarly found to be unchanged after standing two months. Attempts to prepare this ketene by thermal dehydrochlorination were unsuccessful as repeated distillation could not completely free the ketene of the acid chloride. The ketene was readily prepared however by treatment of the acid chloride with triethylamine.

EXPERIMENTAL[5]

Diethyl isopropylidenemalonate was prepared by condensation of acetone with diethyl malonate in the presence of zinc chloride.[6] Treatment of the malonate ester with phenylmagnesium bromide and with methylmagnesium iodide afforded diethyl (α,α-dimethylbenzyl)malonate[7] and diethyl *tert*-butylmalonate,[8] respectively.

α-Carbethoxy-β-phenylisovaleric acid. A filtered solution of ethanolic potassium hydroxide, prepared from 10.1 g. (0.18 mole) of potassium hydroxide, and 200 ml. of absolute ethanol, was added to 50 g. (0.18 mole) of diethyl (α,α-dimethylbenzyl)malonate in 100 ml. of absolute ethanol. After standing at room temperature for 20 hr., the ethanol was removed by distillation at reduced pressure. From the neutral fraction of the products 9.9 g. (20%) of recovered diethyl (α,α-dimethylbenzyl)malonate, b.p. 120–126° at 0.2 mm., n^{24}D 1.4988, was obtained.

From the acid fraction by crystallization from petroleum ether (b.p. 60–70°) was obtained 22.9 g. (51%) of colorless ester-acid, m.p. 57–60°. The analytical sample melted at 59.5–60.5°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.2; H, 7.3. Found: C, 67.3; H, 7.4.

(α,α-Dimethylbenzyl)carbethoxyketene. (*a*) *By thermal dehydrochlorination.* Thionyl chloride (18 g., 0.15 mole) was treated with 25 g. (0.1 mole) of α-carbethoxy-β-phenylisovaleric acid. After standing overnight, the mixture was heated on a steam bath for 1 hr. and then the excess thionyl chloride was removed under reduced pressure. The resulting yellow liquid was twice distilled under reduced pressure to give 21.3 g. (92%) of colorless liquid, b.p. 151–154° at 15 mm., n^{23}D 1.5135. An infrared spectrum (liquid film) showed strong absorption at 4.7 and 5.7 μ, characteristic of the ketene and ester carbonyl functions.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.4; H, 6.9. Found: C, 72.2, 72.4; H, 6.4, 6.7.

In another preparation an infrared spectrum taken prior to distillation showed carbonyl absorption at 5.45 and 5.7 μ, but no ketene absorption at 4.7 μ. Upon distillation, the absorption at 5.45 μ disappeared and that at 4.7 μ appeared. When gaseous anhydrous hydrogen chloride was passed into the liquid ketene, the reverse was noted.

(*b*) *By the triethylamine method.* A solution of crude α-carbethoxy-β-phenylisovaleroyl chloride, prepared as above from 13.5 g. (0.054 mole) of α-carbethoxy-β-phenylisovaleric acid, in 75 ml. of dry benzene was treated with 10.9 g. (0.108 mole) of triethylamine and the mixture allowed to stand for 24 hr. The triethylamine hydrochloride was removed by filtration and the solvent removed under reduced pressure. Distillation afforded 7.3 g. (58%) of colorless liquid, b.p. 145–148° at 13 mm., 1.5138. The infrared spectrum of this material was identical with that above. A small amount of dark viscous material remained after distillation.

tert-Butyl-α-carbethoxyacetic acid.[9] A solution of 86.4 g. (0.4 mole) of diethyl *tert*-butylmalonate in absolute ethanol was treated with an ethanol solution containing 22.4 g. (0.4 mole) of potassium hydroxide. Work-up similar to that described above gave 14.2 g. (16%) of recovered diethyl ester and 55.3 g. (74%) of the desired ester-acid, b.p. 124–127° at 4 mm.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.6. Found: C, 57.7; H, 8.7.

tert-Butylcarbethoxyketene. *tert*-Butyl-α-carbethoxyacetic acid (13.7 g., 0.073 mole) was added to 10 ml. of thionyl chloride and the mixture allowed to stand overnight. After removing the excess thionyl chloride, the acid chloride was taken up in 100 ml. of dry benzene and treated with 15.2 g. (0.15 mole) of triethylamine. This mixture was allowed to stand for 24 hr. and the solid triethylamine hydrochloride was filtered and washed with dry benzene. Distillation of the benzene followed by distillation yielded 9.05 g. (73%) of pale yellow liquid, b.p. 167–172°. A portion was redistilled to give the analytical sample as a colorless liquid, b.p. 168–170°. The infrared spectrum showed strong absorptions at 4.7 and 5.75 μ, indicative of the ketene and ester carbonyl groups.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.5; H, 8.3. Found: C, 63.8, 63.6; H, 8.6, 8.6.

Attempts to prepare the ketene in a pure state by thermal dehydrochlorination were unsuccessful. When the crude acid chloride was distilled at atmospheric pressure a colorless liquid, b.p. 170–178° was obtained. However, the infrared

---

(2) For a review on ketenes, see W. E. Hanford and J. C. Sauer, *Org. Reactions*, **III**, 108 (1946).

(3) H. Staudinger and St. Bereza, *Ber.*, **42**, 4908 (1909).

(4) H. Staudinger and H. Hirzel, *Ber.*, **50**, 1024 (1917).

(5) All melting and boiling points are uncorrected. Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

(6) A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **60**, 2644 (1938).

(7) F. S. Prout, E. P. Y. Haung, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954).

(8) S. Wideqvist, *Arkiv Kemi*, **23B**, No. 4, 1 (1946).

(9) Kindly prepared by Dr. Jyotirmoy Roy.

spectrum showed the presence of the acid chloride carbonyl absorption (5.5 μ) in addition to that of the ketene grouping. Further distillations of this material did not seem to lessen the amount of acid chloride present.

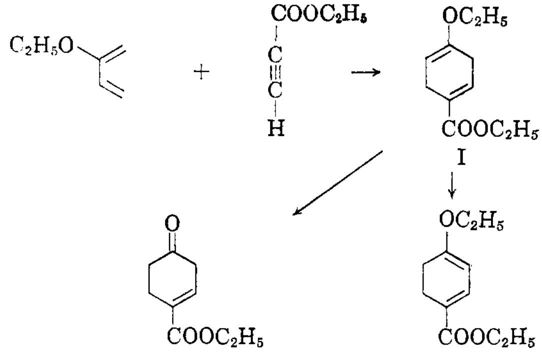
DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

Synthesis of 4-Carbethoxy-3-cyclohexenone

ANESTIS L. LOGOTHETIS AND NORMAN A. NELSON[1]

Received October 2, 1961

On considering the facile alkylation of Hagemann's ester,[2] and hydrolysis and decarboxylation of the intermediate to give 2-alkyl-3-methyl-2-cyclohexenones, we became interested in the preparation and alkylation of 4-carbethoxy-3-cyclohexenone (II) as a possible route to 2-alkyl-2-cyclohexenones.



The Diels-Alder reaction of 2-ethoxy-1,3-butadiene and ethyl propiolate gave 70% of material that was chiefly ethyl 4-ethoxy-2,5-dihydrobenzoate (I). The structural assignment of this compound is based partly on the fact that dienes with substituents in the 2-position are known to yield exclusively 1,4-disubstituted adducts with monsubstituted dienophiles.[3] Also when the product was treated with palladium-on-charcoal in refluxing xylene and then hydrolyzed, 4-ethoxybenzoic acid was obtained. The ultraviolet spectrum of the adduct, $\lambda_{max}^{C_2H_5OH}$ 256 mμ (ε 3640), 320 (sh) mμ (ε 1450), indicates that the product is chiefly the unconjugated diene I, with about 12% of the conjugated diene III. The absorption at 256 mμ is suggestive that some ethyl 4-ethoxybenzoate [$\lambda_{max}^{C_2H_5OH}$ 259 mμ (ε 10,500)] is present; however, that such is not the case was demonstrated by isomerization to ethyl 4-ethoxy-2,3-dihydrobenzoate (III), $\lambda_{max}^{C_2H_5OH}$ 322 mμ (ε 11,500), in 88% yield by the use of sodium ethoxide in ethanol at room temperature, with the concomitant loss of the absorption maximum at 256 mμ.[4] Selective hydrolysis of the Diels-Alder adduct with aqueous acid gave 4-carbethoxy-3-cyclohexenone II (71%) as a colorless liquid. The double bond has been assigned to the 3- position on the basis of the presence of only one carbonyl absorption peak in the infrared spectrum, $\lambda_{max}^{CCl_4}$ 1725 cm.$^{-1}$, (conjugated ester and unconjugated ketone carbonyls),[5] and the ultraviolet spectrum, $\lambda_{max}^{C_2H_5OH}$ 215 mμ (ε 8300) (typical of α,β-unsaturated esters).[6] This compound (II) absorbed one mole of hydrogen on catalytic hydrogenation over 10% palladium-on-charcoal catalyst to give presumably 4-carbethoxycyclohexanone characterized as the 2,4-dinitrophenylhydrazone derivative. Attempts to isomerize II to 4-carbethoxy-2-cyclohexenone with sodium ethoxide have failed, the material being transformed instead into high molecular weight condensation products. Alkylation of 4-carbethoxy-3-cyclohexenone (II) with a variety of alkyl halides using sodium ethoxide in ethanol gave mixtures of difficultly separated mono- and dialkylated products in 35–45% yields, the rest of the material being resinous self-condensation products. Due to a pending change of laboratories, no further attempts were made to study other alkylation conditions and no further work in this area is anticipated.

EXPERIMENTAL[7]

Ethyl 4-ethoxy-2,5-dihydrobenzoate (I). A mixture of 63.5 g. of 2-ethoxy-1,3-butadiene,[3d] 63.5 g. of ethyl propiolate,[8] 650 ml. of anhydrous benzene, and 0.2 g. of hydroquinone was heated in an autoclave at 140° for 24 hr. Distillation of the mixture under reduced pressure gave 88.4 g.

---

[1] Department of Chemistry, the Upjohn Co., Kalamazoo, Mich.

[2] L. E. Smith and G. F. Rouault, *J. Am. Chem. Soc.*, **65**, 631 (1943); E. Bergmann and A. Weizmann, *J. Org. Chem.*, 4, 266 (1939); A. J. B. Edgar, S. H. Harper, and M. A. Kazi, *J. Chem. Soc.*, 1083 (1957).

[3] (a) K. Alder, M. Schumacher, and O. Wolff, *Ann.*, **564**, 79 (1949); (b) K. Alder and W. Vogt, *Ann.*, **564**, 120 (1949); (c) K. Alder and M. Schumacher, "Fortschritte der Chemie Organischer Naturstoffe," Vol. X, Wien-Springer Verlag, Vienna, Austria, 1953, p. 21; (d) E. A. Braude, E. R. H. Jones, F. Sondheimer, and J. B. Toogood, *J. Chem. Soc.*, 607 (1949).

[4] Ultraviolet spectra of similar systems for example, 2,5-dihydroacetophenone $\lambda_{max}^{C_2H_5OH}$ 245 mμ (ε 4000), 2,5-dihydro-6-methylacetophenone $\lambda_{max}^{C_2H_5OH}$ 245 mμ (ε 5000), 4-ethoxy-2,5-dihydroacetophenone $\lambda_{max}^{C_2H_5OH}$ 228 mμ (ε 11,500), and 4-ethoxy-2,3-dihydroacetophenone $\lambda_{max}^{C_2H_5OH}$ 336 mμ (ε 13,000), have been reported by E. A. Braude and coworkers.[3d]

[5] L. G. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Edition, John Wiley and Sons, Inc., New York, 1958, pp. 132–136, 179–182.

[6] A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

[7] Melting points were determined by the use of a hot stage microscope and are corrected. Boiling points are uncorrected. The infrared spectra were determined with a Baird (Model B) spectrophotometer fitted with a sodium chloride prism, and the ultraviolet spectra were determined with a Cary recording spectrophotometer (Model 11 MS). The analyses were performed by Dr. S. M. Nagy and his associates.

[8] W. H. Perkin, Jr., and J. L. Simonsen, *J. Chem. Soc.*, **91**, 833 (1907).