10.1 g (0.10 mol) of triethylamine were taken up in a mixture of 100 ml of benzene and 25 ml of ether, and cooled to 0° with stirring under N_2.

A solution of 20 g (0.10 mol) of α-bromoacetophenone in 60 ml of benzene was added dropwise over 1 hr, and the reaction mixture was allowed to warm to room temperature. Filtration to remove triethylamine hydrobromide and treatment of the filtrate with dry hydrogen chloride yielded the crude hydrochloride salt of the product as a syrup. Recrystallization from 2-propanol afforded 8.0 g (35%) of the salt as an off-white solid, mp 170–172°.

Samples of the free base for photolysis were secured by ether extraction of a basic aqueous suspension of the salt. The final product was a yellow oil: ir 5.90 (s), 6.18 (s); nmr δ 8.0–7.5 (m, 5 H), 5.98 (s, 2 H), 4.16 (s, 2 H), 3.70 (s, 4 H).

This compound is very susceptible to oxidation to *N*-phenacylpyrrole, and gave unsatisfactory elemental analyses. Its high-resolution mass spectrum showed a parent ion at *m/e* 187.0994 (calcd 187.0997).

Photolyses.—The phenacylamine salts were irradiated in 100-mg quantities as 1% solution in 1:99 water–methanol with a Pyrex-filtered 450-W Hanovia source; the free allylamine derivatives were irradiated as 1% benzene solution in a Rayonet "merry-go-round" apparatus using 3000-Å lamps. Irradiations were carried out in an atmosphere of purified nitrogen.

Products were isolated by preparative gas phase chromatography of the photolysis reaction mixtures following removal of solvent by atmospheric pressure distillation.

Registry No.—Ic, 33777-39-8; Id, 33777-40-1.

Acknowledgment.—The author is grateful to Dr J. S. Swenton for suggestions and use of laboratory facilities during the course of this work. J. A. H. acknowledges an Ohio State University predoctoral fellowship, 1970.

α Anions of Carboxylic Acids. V. A Simple High Yield Presentation of α-Alkylhydracrylic Acids and α-Alkylacrylic Acids[1]

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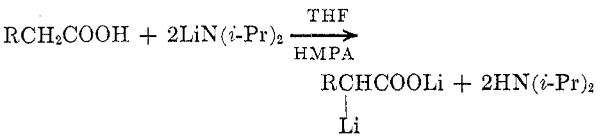
The facile preparation of α-metalated carboxylate salts (dianions) (I) (eq 1) has provided unique opportunities for derivatizing long-chain fatty acids at the α-methylene carbon.[3–5]



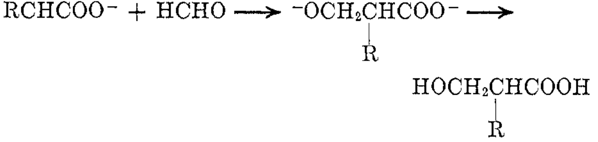
$$\mathrm{RCH_2COOH} + 2\mathrm{LiN}(i\text{-}\mathrm{Pr})_2 \xrightarrow[\mathrm{HMPA}]{\mathrm{THF}} \mathrm{R}\underset{\substack{|\\ \mathrm{Li}}}{\mathrm{C}}\mathrm{HCOOLi} + 2\mathrm{HN}(i\text{-}\mathrm{Pr})_2 \quad (1)$$

I

The reaction of α-metalated carboxylate salts with formaldehyde is shown in this report to be a facile, high-yield synthesis of α-alkylhydracrylic and α-alkylacrylic acids. Prior to this development, low-molecular-weight derivatives of both classes of compounds were inconveniently prepared by multistep reactions, generally in low yields (20–60%).[6] Several single-step syntheses have been described in the patent literature, although yields in general never exceed 20%.[7]

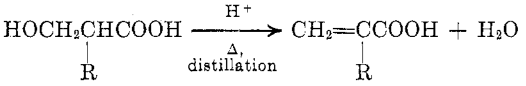
The synthesis of β-hydroxy acids or esters by reaction of carbonyl compounds with metalated carboxylic acids or esters has been previously reported by other investigators.[8–10] However, the reaction of formaldehyde was not included among their aldehydes examined, an omission that would have provided the key hydracrylic acid intermediates—the primary methylol derivatives—for convenient preparations of α-alkylacrylic acids.

The initial reaction of formaldehyde with the metalated carboxylates produces α-alkylhydracrylic acids (II) (eq 2) and the latter compounds are readily dehydrated by acid catalyst to α-alkylacrylic acids (III) (eq 3). The α-alkylacrylic acids (III) are advantageously distilled from the reaction zone during the dehydration process. In the present development, each of the two classes of derivatives is isolated in yields generally exceeding 90%.



$$\mathrm{R\bar{C}HCOO^-} + \mathrm{HCHO} \longrightarrow {}^-\mathrm{OCH_2}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}\mathrm{HCOO^-} \xrightarrow{\mathrm{H^+}} \mathrm{HOCH_2}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}\mathrm{HCOOH} \quad (2)$$

II



$$\mathrm{HOCH_2}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}\mathrm{HCOOH} \xrightarrow[\Delta,\ \text{distillation}]{\mathrm{H^+}} \mathrm{CH_2{=}}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}\mathrm{COOH} + \mathrm{H_2O} \quad (3)$$

III

The advantages of using hexamethylphosphoramide (HMPA) as a cosolvent in tetrahydrofuran (THF) solution for solubilizing salts and dianions of low solubility has been demonstrated for several reactions.[4,5] Recent reports on alkylations of dianions[11,12] have indicated that mixed cationic species of metalated carboxylates, *e.g.*, $[\mathrm{LiNa}]^{2+}$, impart improved reactivity to dianions compared to the dilithiated salts and that heterogeneity due to poorly solubilized dianions is not a barrier to a successful reaction.[12,13] The use of mixed cations would provide an alternative to the use of HMPA, were the advantages of the former found to be general for reactions other than alkylations. In order to determine the relative merits of mixed cations and HMPA in the formylation reactions, the

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[1] Paper IV: P. E. Pfeffer and L. S. Silbert, *J. Org. Chem.*, **36**, 3290 (1971).

[2] Eastern Marketing and Nutrition Research Division, Agriculture Research Service, U. S. Department of Agriculture.

[3] P. L. Creger, *J. Amer. Chem. Soc.*, **89**, 2500 (1967).

[4] P. E. Pfeffer and L. S. Silbert, *J. Org. Chem.*, **35**, 262 (1970).

[5] P. E. Pfeffer, L. S. Silbert, and J. M. Chirinko, Jr., *J. Org. Chem.*, **37**, 451 (1972).

[6] (a) S. Reformatsky, *J. Prakt. Chem.*, 469 (1896); (b) C. Mannich and K. Ritsert, *Ber.*, **57B**, 1116 (1924); (c) K. Chikanishi and T. Tsuruta, *Makromol. Chem.*, **81**, 198 (1965); (d) C. F. Allen and M. J. Kalm, "Organic Syntheses, Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 616; (e) Y. Yamashita, H. Kato, K. Hisano, T. Ito, and M. Hasegawa, *Kogyo Kagaku Zasshi*, **65**, 2050 (1962); *Chem. Abstr.*, **58**, 12774*e* (1963).

[7] (a) B. C. Redmon, U. S. Patent 2,734,074 (Feb 7, 1956); (b) T. A. Koch and I. M. Robinson, U. S. Patent 3,014,958 (Dec 26, 1961); (c) J. M. Leathers and G. E. Woodward, U. S. Patent 3,051,747 (Aug 28, 1962); (d) V. A. Sims and J. F. Vitcha, U. S. Patent 3,247,248 (Apr 19, 1966).

[8] B. Angelo, *C. R. Acad. Sci., Ser. C*, **270**, 1471 (1970).

[9] G. W. Moersch and A. R. Burkett, *J. Org. Chem.*, **36**, 1149 (1971).

[10] M. W. Rathke, *J. Amer. Chem. Soc.*, **92**, 3222 (1970).

[11] P. L. Creger, *ibid.*, **92**, 1396 (1970).

[12] P. L. Creger, *Org. Syn.*, **50**, 58 (1970).

[13] These assertions appear to have a limited validity for alkylations of some dianions. The opposed arguments are discussed in more detail in a former paper (see ref 5).

TABLE I

YIELDS AND PROPERTIES OF α-ALKYLHYDRACRYLIC ACIDS, $HOCH_2C(R)HCOOH$. REACTION OF α ANIONS WITH FORMALDEHYDE

Starting acid	Registry no.	R	Mp or bp, °C (mm)	Yield,[a] % THF	Yield,[a] % THF-HMPA[b]
Hexanoic	33785-85-2	Butyl	114–116 (10)[c]	97	
Nonanoic	33785-86-3	Heptyl	47–48[d]		
			88 (0.3)[c]	96, 65,[e] 12[f]	90, 31[f]
Tetradecanoic	33785-87-4	Dodecyl	75–75.3		89
Hexadecanoic	33785-88-5	Tetradecyl	81–81.7		85,[g] 61
Octadecanoic	33785-89-6	Hexadecyl	85.5–87.0	29	80[g]
cis-9,10-Octadecenoic	33780-97-1	*cis*-7,8-Hexadecenyl	*h*		93
Phenylacetic[i]	529-64-6	Phenyl	117–118[j]		93

[a] Yields determined by glc. All purified products analyzed satisfactorily by elemental analysis, nmr, and mass spectra. [b] One mole of hexamethylphosphoramide (HMPA) per mole of carboxylic acid in tetrahydrofuran (THF) except where indicated. [c] Methyl ester. [d] Lit. mp 47–48°: E. E. Blaise and A. Luttringer, *Bull. Soc. Chim. Fr.*, **33**, 635 (1905). [e] Dianion present in reaction with [LiNa]$^{2+}$ mixed cations; prepared from the sodium salt of the carboxylic acid. [f] Dianion present in reaction with [LiK]$^{2+}$ mixed cations; prepared from the potassium salt of the carboxylic acid. [g] 2 mol of HMPA. [h] Methyl ester decomposes on distillation to a mixture of unsaturated acid and esters. [i] Included as a representative example of an aromatic preparation. [j] Lit. mp 116–117°: A. McKenzie and J. K. Wood, *J. Chem. Soc.*, **115**, 828 (1919).

formylations of dianions with varied counterions were carried out in the presence and absence of HMPA.

α-Alkylhydracrylic Acids.—The results of these preparations are assembled in Table I and show the importance of conducting the formylations in homogeneous solutions to attain high yields of α-alkylhydracrylic acids. Short-chain dianions such as dilithiated nonanoate are sufficiently soluble in THF in the absence of HMPA to achieve an efficacious formaldehyde reaction (96% yield), whereas long-chain dianions such as octadecanoate require dissolution by HMPA for successful formylations (80% in HMPA *vs.* 29% without HMPA). The results also highlight the importance of the counterion type, since yields diminish in the order [LiLi]$^{2+}$ (96%) > [LiNa]$^{2+}$ (65%) > [LiK]$^{2+}$ (12%). These results are explained in part by the low solubility of the [LiNa]$^{2+}$ and [LiK]$^{2+}$ dicationic species in THF solutions, indicating a slow progressive reaction between formaldehyde and the heterogeneous phase of the metalated carboxylates. It is evident from the example of α-heptylhydracrylic acid (Table I) that yields increase as the solubility of the mixed salt species, *e.g.*, [LiK]$^{2+}$, is increased by inclusion of HMPA as cosolvent, thereby providing a convincing argument for carrying out dianion reactions in homogeneous solutions.

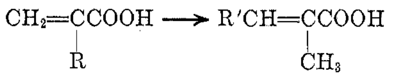
α-Alkylacrylic Acids.—Dehydration of an α-alkyl hydracrylic acid is conveniently carried out in a distillation flask for subsequent *in vacuo* distillation of the α-alkylacrylic acid. The α-alkylhydracrylic acid containing one drop of phosphoric acid as catalyst is heated *in vacuo* at 180° for 30 min to promote formation of estolides (intermolecular polyesters of undetermined size), the presence of which was indicated by their ir spectra. Elevation of the temperature to 270° pyrolyzed the estolides, and the dehydrated product was distilled at reduced pressure. Distillation of the acrylic acids during the dehydration process is essential to effect a disproportionation of estolide to olefinic acid and hydroxy acid as well as to minimize destruction of the liberated products by the acid catalyst. Excellent yields of isomerically pure α-alkylacrylic acids (Table II) are simply obtained. Absence of isomer IV as a possible product by isomerization of III (eq 4) was indicated by glc and nmr analysis.

TABLE II

α-ALKYLACRYLIC ACID PREPARATION *via* DEHYDRATION OF α-ALKYLHYDRACRYLIC ACIDS, $HOCH_2C(R)HCOOH$. YIELD AND PROPERTIES OF α-ALKYLACRYLIC ACIDS, $CH_2{=}C(R)COOH$

R	Registry no.	α-Alkylacrylic acid Mp or bp, °C (mm)	α-Alkylacrylic acid Yield,[a] %
Butyl	4380-88-5	111–113 (10)[b]	94
Heptyl	1118-91-8	122 (0.5)[c]	94, 70,[d] 79[e]
Dodecyl	33785-92-1	44–45	
		157 (0.2)	90
Tetradecyl	6818-50-4	55–55.8	84
Hexadecyl	6818-51-5	60–61.0	
		205–209 (0.25)	90
cis-7,8-Hexadecenyl	33780-98-2	196–197 (0.4)	90

[a] Yields determined on distilled product by glc. All products analyzed satisfactorily by glc, elemental analysis, nmr, and mass spectra. [b] Lit. bp 109–110° (10 mm): E. E. Blaise and A. Luttringer, *Bull. Soc. Chim. Fr.*, **33**, 760 (1905). [c] Lit. bp 128–134° (2 mm): Y. Yamashita, H. Kato, K. Hisano, T. Ito, and M. Hasegawa, *Kogyo Kagaku Zasshi*, **65**, 2050 (1962); *Chem. Abstr.*, **58**, 12774e (1963). [d] Uncatalyzed dehydration. [e] Sulfuric acid catalyzed dehydration.



$$\underset{\text{III}}{CH_2{=}\underset{R}{C}COOH} \longrightarrow \underset{\text{IV}}{R'CH{=}\underset{CH_3}{C}COOH} \qquad (4)$$

III IV

Thermal dehydration of α-alkylhydracrylic acids by use of sulfuric acid as catalyst or in the absence of catalyst results in lower product yields. Dehydrations by means of sulfuric acid as catalyst are accompanied by excessive charring, while in the absence of catalyst prolonged reaction times are required.

Experimental Section

Tetrahydrofuran, hexamethylphosphoramide, and diisopropylamine were purified as previously described.[4,5]

Paraformaldehyde was dried over phosphorus pentoxide before use.

Sodium and potassium salts of carboxylic acids were crystallized from methanol–THF, dried at 110° for 12 hr, and stored in a desiccator over phosphorus pentoxide.

Purity of methyl esters of acrylic and hydracrylic acid derivatives was examined by glc [Dow Corning 710 silicone oil (10%)].

Preparation of 2-Heptylhydracrylic Acid.—The following preparation of 2-heptylhydracrylic acid and 2-heptylacrylic acid typifies the general procedures for preparing these classes of compounds. Preparation of α-metalated carboxylate salts has been described in previous papers.[4,5]

Paraformaldehyde (8 g) was heated at 180–200° to generate formaldehyde[14] and the formaldehyde vapors were carried by a stream of N_2 over the surface of a stirred THF solution (50 ml) of α-lithiated lithium nonanoate (3.28 g, 0.02 mol) containing 1 molar equiv of HMPA. The reaction was terminated after complete depolymerization of paraformaldehyde. The reaction solution was cooled in an ice bath and neutralized with dilute (10%) hydrochloric acid until acidic. The aqueous layer was separated and extracted with ethyl ether. To ensure complete removal of HMPA, the ether layer was extracted with four portions of dilute hydrochloric acid. The ether layer was dried and α-heptylhydracrylic acid was recovered by evaporation of solvent, yield 2.85 g (90%). The crude product was purified by crystallization from acetonitrile.

Other similarly prepared α-alkylhydracrylic acids (Table I) were purified by crystallization (solvent in parenthesis): α-dodecyl, α-tetradecyl, and α-hexadecyl (hexane); α-phenyl (ethyl alcohol). α-Butylhydracrylic acid was distilled in vacuum.

Preparation of 2-Heptylacrylic Acid.—2-Heptylhydracrylic acid (2.0 g, 0.01 mol) and phosphoric acid (one drop) were stirred in a R.B. flask (10 ml) equipped with a short-path distillation head and heated to 180° in a Wood's metal bath under vacuum (0.5 mm) for 30 min. The temperature was raised to 270° to decompose the estolides and to distil pure 2-heptylacrylic acid (head temperature, 122°), yield 1.7 g (94%). The long-chain derivatives were also recrystallized, 2-dodecylacrylic acid from hexane and 2-tetradecyl- and 2-hexadecylacrylic acids from acetone. Table II records properties and yields.

Registry No.—Formaldehyde, 50-00-0.

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[14] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 397.

Investigations on Vinylogous Fries and Photo-Fries Rearrangements[1]

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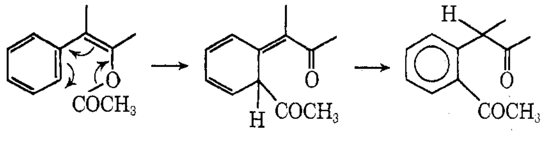
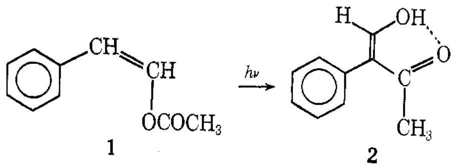
Received September 29, 1971

The photo-Fries rearrangement has been widely investigated and extended to simple vinyl esters,[2] as well as to the 1,3-dienyl acetate system, which is reported to undergo both 1,3- and 1,5-acyl migration.[3] The latter finding raises questions concerning the photoreactivity of β-phenyl vinyl acetate derivatives which may *a priori* undergo 1,3-acyl migration as a simple vinyl system or 1,5 migration to the ortho ring position, which would constitute a vinylogous Fries rearrangement (eq 1), a new reaction of potential synthetic and mechanistic importance. Furthermore, this prospect prompted studies on the thermal reactivity of this system which were carried out both in the presence and absence of Lewis acids.



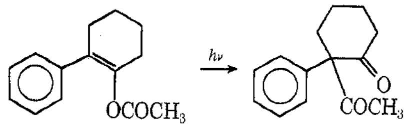
(1)

Irradiation (254 nm) of phenylacetaldehyde enol acetate (1), as a mixture of the cis and trans isomers,[4] in benzene or acetonitrile solution, yielded the known α-acetyl phenylacetaldehyde (2)[5] as the only apparent primary photoproduct, which was determined by monitoring (glc) the reaction at less than 5% conversion with the use of an internal standard. Throughout the reaction course, no additional products were in evidence in significant amounts, although 2 was found to be photolabile and attained a maximum concentration of about 25%. The product 2, mp 69–70°, was isolated by silica gel chromatography and characterized by elemental and spectral analysis (see Experimental Section). This result parallels the known photorearrangement of β-phenyl enamides, which also undergo 1,3-acyl migration.[6]



1 **2**

With the hope of enhancing the prospect of 1,5-acyl migration, the photochemistry of 1-acetoxy-2-phenylcyclohexene (3)[7] was also investigated, in which case (1) the phenyl and acetoxy groups are fixed in the requisite cis configuration for concerted migration, and (2) 1,3 migration is sterically more hindered. However, only the product of 1,3 migration, the previously unknown 2-acetyl-2-phenylcyclohexanone (4), was produced together with small amounts of 2-phenylcyclohexanone. The assignment of structure 4 was readily deduced from elemental and spectral analysis (see Experimental Section).



3 **4**

In the absence of Lewis acids, this system was found to be remarkably heat stable. Both 1 and 3 were quantitatively recovered after being heated in benzene or acetonitrile solution at 550° for 30 min in sealed tubes, as evidenced by glc and infrared analysis. Compound 3 remained essentially unchanged on passage through a Vycor tube packed with glass helices (1 × 25 cm) at 750°. On the other hand, when the helices were packed to a height of 50 cm, only trace amounts of starting material and volatile products were detected.

On heating 3 at 210° in benzene together with an equimolar amount of boron trifluoride etherate and an internal standard, slow decomposition occurred (about 50% in 1.5 hr); however, only trace amounts of products could be detected by glc analysis, suggestive of a polymerization process. The bulk of the material was apparently polymerized, as well, on treatment of 3 under standard Fries conditions with aluminum chlo-

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Taken in part from the Ph.D. thesis of J. E. A., North Dakota State University.

[2] (a) V. I. Stenberg in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 127–153; (b) D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967).

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[5] H. Yasuda, *Yakugaku Zasshi*, **79**, 623 (1959); *Chem. Abstr.*, **53**, 21885e (1959).

[6] R. W. Hoffmann and K. R. Eicken, *Tetrahedron Lett.*, 1759 (1968).

[7] A. N. Kost and I. P. Sugrobova, *Vestn. Mosk. Univ., Ser. II*, **18**, 75 (1963); *Chem. Abstr.*, **59**, 7460d (1963).