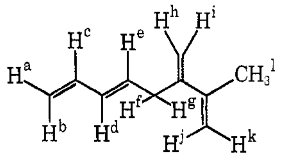
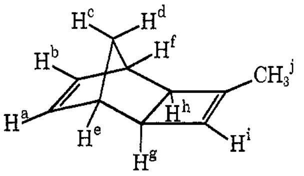
hexene and 1,3,7-octatriene[4] were also observed. These competing reactions consumed almost all the excess butadiene. When isoprene or 1,3-pentadiene was used in this reaction, only the corresponding dimers could be isolated.



1

A similar study of the reaction of allene with bicyclo[2.2.1]hepta-2,5-diene was made. Under conditions similar to those applied to butadiene, a *ca.* 25% yield of *exo*-3-methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**2**) was obtained.



2

The preparation appeared to yield a single isomer and differentiation between the two possible ring junction isomers was made possible by an analysis of the nmr spectrum. Spin decoupling of the pairs H^a, H^e and H^b, H^f verified the assignments of H^e and H^f. Computer simulation[5] of the region containing the H^{e-h} protons gave a closest fit with $J_{g,h} \cong 4$; $J_{e,g} = J_{f,h} \leqslant 2$ and $J_{g,i} \cong 0.5$ Hz. The second coupling constant, in the cases of *endo*- and *exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene, has been reported[6] to be 3.5 and $\leqslant 1$ Hz, respectively. Also, the proton chemical shifts reported for the latter isomer closely resembled comparable shifts found with **2**. Hence, we have assigned the exo configuration to the reaction product. Catalytic hydrogenation of **2** gave a single, saturated hydrocarbon following an uptake of 2.04 equiv of hydrogen.

Substantial amounts of an impure, higher boiling material [bp 53–54° (0.12 mm)] were also isolated from the reaction. Although elemental analysis suggested a 2:1 allene–bicyclo[2.2.1]hepta-2,5-diene adduct, a complete structural assignment was thwarted by the lack of sufficiently pure material.

It may be noted that **2** could conceivably arise from a cycloaddition of methylacetylene, formed *in situ* from allene, to bicyclo[2.2.1]hepta-2,5-diene.[7] However, no evidence for the formation of **2** was found upon substitution of methylacetylene for allene in the reaction.

Experimental Section

Boiling points are uncorrected. The relative proton intensities, determined by nmr, may be assumed to be within ±3% where not noted otherwise.

trans- **and** *cis*-**2-Methyl-3-methylene-1,5,7-octatriene** (**1**).—A solution of bis(triphenylphosphine)(maleic anhydride)palladium (1.47 g, 0.002 mol) in 25 ml of tetrahydrofuran was charged to a 400-cc stainless steel lined autoclave. To this solution was added allene (20 g, 0.50 mol) and butadiene (162 g, 3.0 mol). The mixture was heated to 120° for 5 hr with stirring. The resulting liquid was directly distilled giving a fraction of bp 45–100° (16 mm). Redistillation of this crude fraction through a 24-in. spinning-band column gave **1** (14.8 g, >90% purity, 39% yield). A pure sample was prepared by glc collection: bp 67.5–69° (16 mm); ir (neat) 1595, 1630, and 1650 cm^{-1} (C=C); uv (ethanol) λ_{max} 225 mμ (ϵ 35,600); nmr (220 MHz, CCl_4) δ 1.88 (H^l, s), 2.97 (H^f, H^g, d, J = 7 Hz, trans), 3.08 (H^f, H^g, d, J = 7 Hz, cis), 4.82–5.20 (H^a, H^b, H^h, H^i, H^j, H^k, m), 5.40–6.65 (H^c, H^d, H^e, m, $J_{c,d,cis}$ = 9 Hz, $J_{c,d,trans}$ = 14 Hz).

Anal. Calcd for $C_{10}H_{14}$: C, 89.50; H, 10.51. Found: C, 89.60; H, 10.60.

Hydrogenation of *trans*- **and** *cis*-**2-Methyl-3-methylene-1,5,7-octatriene** (**1**).—A sample of **1** (1.34 g, 0.0097 mol, >97% purity) and 5% palladium on charcoal (0.1 g) were mixed with 10 ml of absolute ethanol and exposed to hydrogen with stirring. The mixture absorbed 944 ml of hydrogen. The mixture was filtered to remove catalyst and the solvent was evaporated from the filtrate to give 1.2 g of colorless liquid. Glc purification of this material gave a liquid which had an infrared spectrum and a glc retention time identical with that of an authentic sample of 2,3-dimethyloctane.

exo-**3-Methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene** (**2**).—A solution of bicyclo[2.2.1]hepta-2,5-diene (660 ml, 6.57 mol) and bis(triphenylphosphine)(maleic anhydride)palladium (8.75 g, 0.01 mol) was charged to a 1000-ml stainless steel lined autoclave. The system was then charged with allene (57.5 g, 1.40 mol) and heated to 145° for 5 hr. The resulting solution was distilled through a 24-in. spinning-band column, giving **2** (45.6 g, 25% yield): bp 49–50.5° (16 mm); ir (neat) 1630, 1590, and 1561 cm^{-1} (C=C); nmr (220 MHz, CCl_4) δ 1.31 (H^c, H^d, AB pattern, $J_{c,d}$ = 8 Hz), 1.67 (H^j, s), 2.18 and 2.15 (H^g and H^h, s), 2.32 (H^e, H^f, m), 5.85 (H^i, s), 6.00 (H^a, H^b, s).

Anal. Calcd for $C_{10}H_{12}$: C, 90.8; H, 9.20. Found: C, 90.67; H, 9.26.

Hydrogenation of *exo*-**3-Methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene** (**2**).—A mixture of **2** (0.661 g, 0.005 mol) and 0.05 g of 5% palladium on charcoal in 5 ml of ethanol was exposed to 1 atm of hydrogen with stirring. A total of 252.2 ml of hydrogen was absorbed. Filtration and evaporation of the ethanol gave an oil which appeared to be a single compound by glc analysis (retention time 17 min, on 20% silicone gum nitrile, 4 ft × 1/4 in., 78°). Glc collection afforded a pure sample: nmr (60 MHz, CCl_4) δ 1.6–3.3 (m, 7 protons), 0.8–1.6 (m, 9 protons).

Anal. Calcd for $C_{10}H_{16}$: C, 88.25; H, 11.85. Found: C, 88.64; H, 12.22.

Registry No.—*trans*-**1**, 33885-13-1; *cis*-**1**, 33885-14-2; **2**, 33885-15-3; hydrogenation product of **2**, 33885-16-4; palladium, 7440-05-3; allene, 463-49-0; bicyclo[2.2.1]-hepta-2,5-diene, 121-46-0; butadiene, 106-99-0.

Acknowledgment.—I thank Dr. Raymond C. Ferguson for the nmr simulation studies.

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[4] E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1967).

[5] A five-spin approximation using a modified LAOCOON-type program developed by C. W. Haigh, University College, Swansea, Wales.

[6] (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 623 (1966); (b) L. G. Cannell, *Tetrahedron Lett.*, **No. 48**, 5967 (1966).

[7] G. N. Schrauzer and P. Glockner, *Chem. Ber.*, **97**, 2451 (1964).

Photochemical Conversion of Primary and Secondary Amines to Carbonyl Compounds

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Received August 16, 1971

The occurrence of the Norrish type II elimination as the major process[1] in the photolysis of α-phenacylamines prompted an investigation of the utility of this reaction in effecting the conversion of amines to car-

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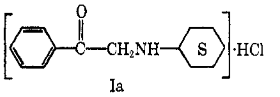
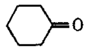
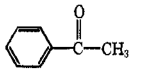
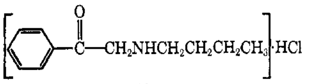
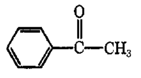
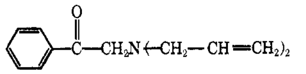
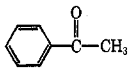
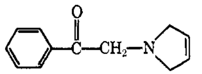
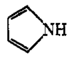
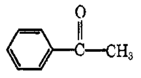
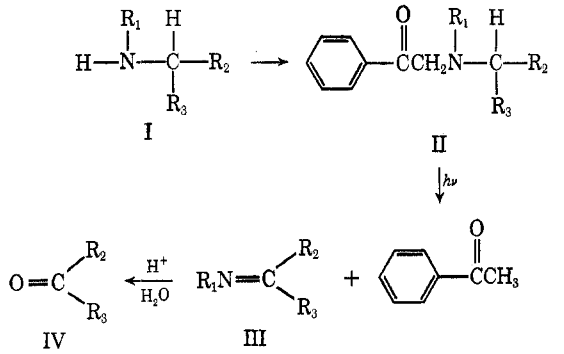
[1] A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 1857 (1969).

TABLE I

Starting material	Product	Yield, %	Other product	Solvent	Irradiation time, hr	Conversion, %
 Ia		71		1% H_2O in CH_3OH	28	60
 Ib	$CH_3CH_2CH_2CHO$	57		1% H_2O in CH_3OH	13	35
 Ic		90	Polymer	C_6H_6	7	100
 Id		92		C_6H_6	5	100

bonyl compounds. We wish to report here that the photolysis of phenacyl derivatives of primary and secondary amines is a preparatively useful method for the conversion of the amino group to a carbonyl function under mild, nonoxidative conditions.

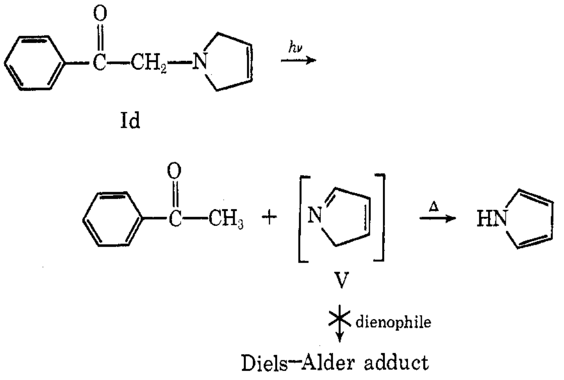
The instability of *N*-phenacyl derivatives of primary amines (II, $R_1 = H$) relative to dihydropyrazines[2] requires the isolation and use of these compounds as their salts. It is demonstrated here that photolysis of these salts proceeds cleanly with formation of Norrish type II products; *in situ* hydrolysis of the imine photoproduct III yields the desired carbonyl compound[3] (eq 1). Results typical of the photolysis of some *N*-phenacylamines are given in Table I.



(1)

As noted in Table I, photolysis of the hydrochloride salts proceeds slowly, but no competing reactions are observed. Shorter irradiation times suffice to give complete conversion of free allylamine derivatives such as *N*-phenacyldiallylamine and *N*-phenacyl-3-pyrroline, however.

Production of pyrrole in the photolysis of *N*-phenacyl-3-pyrroline intimates the transient existence of the valence-bond tautomer V of pyrrole (eq 2). However, all attempts to trap the tautomer as a Diels–Alder adduct (maleic anhydride, dimethylacetylene dicarboxylate, and dichloroethylene, *in situ* and added after irradiation at ambient and low temperatures) failed to give identifiable products other than pyrrole and acetophenone. The lack of Diels–Alder reactivity of heterodienes of the type N=C–C=C has been noted.[5]



(2)

Experimental Section[6]

***N*-Phenacylcyclohexylamine Hydrochloride.**—Material prepared according to the procedure of Cromwell and Mercer[7] and recrystallized from ethanol had mp 252–253° (lit.[7] mp 250–252°).

***N*-Phenacyl-*n*-butylamine Hydrochloride.**—Material prepared according to Hyde, *et al.*,[8] and recrystallized from acetone–ethanol had mp 223–225° (lit.[8] mp 214–215°).

***N*-Phenacyldiallylamine.**—Freshly distilled diallylamine (32 g, 0.34 mol) was dissolved in a mixture of 70 ml of ether and 40 ml of benzene, cooled to 0°, and stirred.

A solution of 32 g (0.16 mol) of α-bromoacetophenone in a mixture of 50 ml of ether and 20 ml of benzene was added dropwise to the diallylamine solution. The stirred reaction mixture was allowed to warm to room temperature when the addition was complete and was finally heated at reflux for 0.5 hr. The precipitate of diallylamine hydrobromide was removed by filtration and the filtrate was treated with dry hydrogen chloride to yield the hydrochloride salt of the product as a syrup.

Treatment of the hydrochloride salt with 50 ml of 15% aqueous NaOH and ether extraction yielded, upon removal of ether *in vacuo*, the desired product as a yellow oil. Distillation through a 4-in. Vigreux column gave 7.0 g (71%) of faintly yellow product: bp 94–95° (0.02 mm); ir 5.90 (s), 6.24 μ (s); nmr δ 8.0–7.5 (m, 5 H), 6.3–5.6 (m, 2 H), 5.4–4.9 (m, 4 H), 3.87 (s, 2 H), 3.27 (broad d, 4 H); mass spectrum *m/e* 215 (parent) (calcd *m/e* 215).

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.78; H, 8.00; N, 6.58.

3-Pyrroline.—Material prepared by the method of Andrews and McElvain[9] had bp 90–91° (lit.[9] bp 89–92°).

***N*-Phenacyl-3-pyrroline.**—3-Pyrroline (6.9 g, 0.10 mol) and

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[2] Y. T. Pratt, *Heterocycl. Compounds*, **6**, 377 (1957).

[3] The possible formation of substituted 3-azetidinols[4] in small amounts was not investigated in this study.

[4] E. H. Gold, *J. Amer. Chem. Soc.*, **93**, 2793 (1971).

[5] A. Oneshchenko, "Diene Synthesis," O. Davey, New York, N. Y., 1964, p 596 ff.

[6] Melting points and boiling points are uncorrected. Ir spectra were taken as Nujol mulls or neat films on a Perkin-Elmer 137 spectrophotometer; nmr spectra were obtained at 60 MHz on a Varian instrument. Mass spectra were determined on an AEI MS-9 instrument. Product mixtures were analyzed and collected by glpc, using SE-30 and PDEAS columns. Microanalyses were performed by W. Rond, The Ohio State University.

[7] H. N. Cromwell and G. D. Mercer, *J. Amer. Chem. Soc.*, **79**, 3815 (1957).

[8] J. F. Hyde, E. Browning, and R. Adams, *ibid.*, **50**, 2287 (1928).

[9] L. H. Andrews and S. M. McElvain, *ibid.*, **51**, 887 (1929).

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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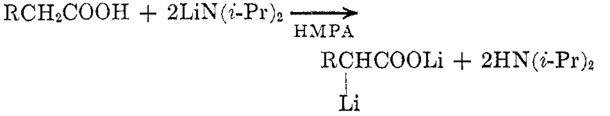
Philadelphia, Pennsylvania 19118

Received September 8, 1971

The facile preparation of α-metalated carboxylate salts (dianions) (I) (eq 1) has provided unique op-



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

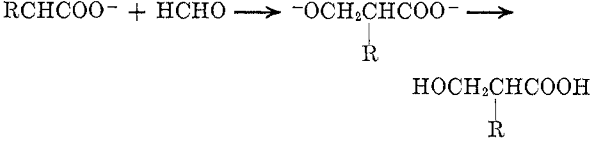
I

portunities for derivatizing long-chain fatty acids at the α-methylene carbon.[3-5]

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.

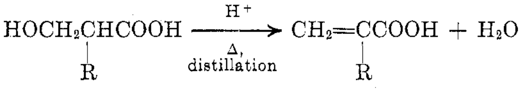
The initial reaction of formaldehyde with the metalated carboxylates produces α-alkylhydracrylic acids (II) (eq 2) and the latter compounds are readily



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

II

dehydrated by acid catalyst to α-alkylacrylic acids (III) (eq 3). The α-alkylacrylic acids (III) are ad-



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

III

vantageously 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%.

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.*, [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).