TABLE I
OXIDATION CONDITIONS AND YIELDS

Substance oxidized	Solvent (ml/g of oxidant)	Product	Bp (mm) or mp, °C Obsd	Bp (mm) or mp, °C Lit	Yield, %
2-Pyridinemethanol[a]	Chloroform (10)	2-Pyridinecarboxaldehyde	68–70 (13–14)	70–73 (13)[b]	68
2-Pyridinemethanol[a]	Benzene (10)	2-Pyridinecarboxaldehyde	68–70 (13–14)		54
3-Pyridinemethanol[a]	Chloroform (10)	3-Pyridinecarboxaldehyde	78–80 (10–11)	86–89 (13)[b]	67
3-Pyridinemethanol[a]	Benzene (10)	3-Pyridinecarboxaldehyde	78–80 (10–11)		78
4-Pyridinemethanol[a]	Chloroform (10)	4-Pyridinecarboxaldehyde[c]	77–78 (11–12)	77–78 (12)[d]	73
4-Pyridinemethanol[a]	Benzene (10)	4-Pyridinecarboxaldehyde[c]	77–78 (11–12)		68
6-Methyl-2-pyridinemethanol[a]	Chloroform (8)	6-Methyl-2-pyridinecarboxaldehyde[e]	71 (11)	70–72 (9)[u]	67
2-Pyridinemethanol 1-oxide[a]	Chloroform (12)	2-Pyridinecarboxaldehyde 1-oxide hydrate	75–77[f]	78–80[g]	62
3-Pyridinemethanol 1-oxide[a]	Chloroform (10)	3-Pyridinecarboxaldehyde 1-oxide[h]	131–133[i]		51
4-Pyridinemethanol 1-oxide[a]	Chloroform (10)	4-Pyridinecarboxaldehyde 1-oxide[j]	149–150	148–150[k]	69
2,6-Pyridinedimethanol[l]	Chloroform (8)	2,6-Pyridinedicarboxaldehyde[m]	122–123	124[n]	54
Imidazole-4-(or 5)-methanol[o,p]	Dioxane (10)	Imidazole-4- (or 5-) carboxaldehyde	174	173–174[p]	59
Benzenethiol	Chloroform (10)	Phenyl disulfide	60	61[q]	92
2-Propene-1-thiol	Chloroform (10)	Allyl disulfide	74–76 (15)	78–80 (16)[q]	66
α-Toluenethiol	Chloroform (10)	Benzyl disulfide	69–70	71–72, 69–70[q]	82
5-Hydroxy-4-octanone	Chloroform (10)	4,5-Octanedione[r]	56–58 (12)	60 (12)[q]	58
4-Hydroxy-3-hexanone	Ethyl ether (10)	3,4-Hexanedione[s]	34–36 (12)	32 (10)[q]	52
N-Phenylhydroxylamine	Water (10)	Nitrosobenzene	64–66	67.5–68[q]	40[t]

[a] From F. Raschig Gmbh., Ludwigshafen. a. Rhein, Germany. [b] See ref 13. [c] Semicarbazone mp 215°; N. Campbell ("Chemistry of Carbon Compounds," Vol IV, Part A, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1957, p 553) reported mp 216°. [d] J. P. Wibaut, E. C. Kooyman, and H. Boer, *Rec. Trav. Chim.*, **64**, 30 (1945). [e] Semicarbazone mp 218°, lit.[2] mp 216°. [f] Recrystallization from benzene raised the melting point to 80°. [g] See ref. 15. [h] *Anal.* Calcd for $C_6H_5NO_2$: C, 58.54; H, 4.09; N, 11.38. Found: C, 58.18; H, 3.94; N, 11.34. Oxime mp 230–231° (recrystallized from 50% ethyl alcohol). *Anal.* Calcd for $C_6H_6N_2O_2$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.40; H, 4.47; N, 20.46. [i] Recrystallized from benzene. [j] Semicarbazone mp 248–250° dec, lit.[k] mp 246–248° dec. [k] S. Furukawa, *Yakugaku Zasshi*, **78**, 957 (1958); *Chem. Abstr.*, **53**, 3219*g* (1959). [l] By reduction of di-*n*-butyl 2,6-pyridinedicarboxylate, purchased from F. Raschig Gmbh. [m] Phenylhydrazone mp 198–199°, lit.[24] mp 199.5°; dioxime mp 212° dec, lit.[24] mp 211.5°. *Anal.* Calcd for $C_7H_7N_3O_2$: C, 50.91; H, 4.27; N, 25.44. Found: C, 50.79; H, 4.12; N, 25.58. [n] See ref 24. [o] J. R. Totter and W. J. Darby, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 460. [p] R. A. Turner, C. F. Huebner, and C. R. Scholz, *J. Am. Chem. Soc.*, **71**, 2801 (1949). [q] See ref 26. [r] Dioxime mp 183°, lit.[26] mp 186–187°. [s] Dioxime mp 190°, lit.[26] mp 185°; semicarbazone mp 271° dec, lit.[26] mp 270° dec. [t] On nitrobenzene. [u] See ref 2.

Experimental Section

All oxidations were carried out at reflux, except for imidazole-4- (or 5-) methanol (dioxane at 80°) and N-phenylhydroxylamine (water at 0°).

The oxidant:substance weight ratio was 5:1 in all but two cases [2,6-pyridinedimethanol and imidazole-4- (or 5-) methanol] where best results were obtained with a 10:1 ratio.

The following two examples illustrate the general experimental procedure.

Oxidation of 2,6-Pyridinedimethanol to 2,6-Pyridinedicarboxaldehyde.—2,6-Pyridinedimethanol was prepared in 58% yield (mp 118°, lit.[21] mp 114–118°) by reduction of di-*n*-butyl 2,6-pyridinedicarboxylate with lithium aluminum hydride following essentially the method described by Jones and Kornfeld[22] and by Mićović and Mihailović.[13]

A suspension of 60 g of freshly prepared manganese dioxide[23] in a solution of 5.7 g of 2,6-pyridinedimethanol in 500 ml of chloroform was stirred at reflux for 5 hr. The mixture was filtered, and the oxide was washed with five 100-ml portions of ether. The combined filtrate and washings were evaporated to dryness under reduced pressure, and the residue was recrystallized from petroleum ether (bp 55–75°) yielding 3 g (54%) of 2,6-pyridinedicarboxaldehyde: mp 122–123°, lit.[24] mp 124°; phenylhydrazone mp 198–199°, lit.[24] mp 199.5°; dioxime mp 212° dec, lit.[24] mp 211.5°.

Anal. (dioxime). Calcd for $C_7H_7N_3O_2$: C, 50.91; H, 4.27; N, 25.44. Found: C, 50.79; H, 4.12; N, 25.58.

Oxidation of N-Phenylhydroxylamine to Nitrosobenzene.—A cold (0°), aqueous solution of N-phenylhydroxylamine was prepared from 30 g (0.244 mole) of nitrobenzene, 15 g of ammonium chloride, 37.2 g of zinc dust, and 850 ml of water.[25] A mixture of this solution with 85 g of manganese dioxide was stirred vigorously at 0° for 3 hr. Steam distillation yielded 10.5 g (40%) of nitrosobenzene, mp 64–66°. One recrystallization from ethyl alcohol raised the melting point to 67–68° (lit.[26] mp 67.5–68°). The infrared spectrum of the product was identical with that of an authentic sample of nitrosobenzene.[25]

Acknowledgment.—The authors wish to thank the Research Corporation and the Arts and Sciences Research Committee of the American University of Beirut for financial support. Thanks are also extended to Dr. M. J. Haddadin for useful discussions and suggestions.

(21) R. A. Barnes and H. M. Fales, *J. Am. Chem. Soc.*, **75**, 3830 (1953).

(22) R. G. Jones and E. C. Kornfeld, *ibid.*, **73**, 107 (1951).

(23) F. Sondheimer, O. Mancera, M. Urquiza, and G. Rosenkranz, *ibid.*, **77**, 4145 (1955).

(24) W. Mathes, W. Sauermilch, and T. Klein, *Ber.*, **86**, 584 (1953).

(25) G. H. Coleman, C. M. McCloskey, and F. A. Stuart, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 668.

(26) I. Heilbron and H. M. Bunbury, Ed., "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953.

A Convenient Preparation of γ-Keto Acids

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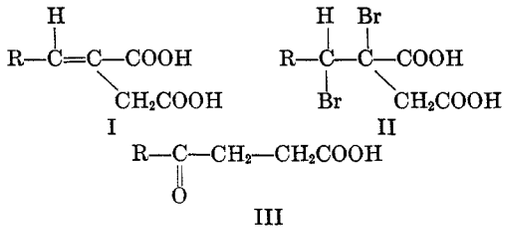
In connection with the studies of γ-lactone derivatives,[1] it has now been found that 3,4-dibromo-3-carboxyalkanoic acids (II)[2] obtained by bromination

(1) K. Sisido, S. Torii, and M. Kawanisi, *J. Org. Chem.*, **29**, 904, 2290 (1964).

(2) (a) R. Fittig and A. Beer, *Ann.*, **216**, 92 (1883); (b) R. Fittig and J. Kraencker, *ibid.*, **331**, 142 (1904); (c) R. Fittig and O. Scheen, *ibid.*, **331**, 137 (1904).

of alkylidenesuccinic acids (I), when treated with hot aqueous alkaline solution, were converted into corresponding γ-keto acids (III) in good yields.



Treatment of 3,4-dibromo-3-carboxydecanoic acid with an excess of 1 *N* alkaline solution at 70–90° for 1 hr afforded γ-ketodecanoic acid in 80–90% yield. The yields of III are listed in Table I. Bromination of I (R = C_5H_{11}, C_6H_{13}, and C_8H_{17}, respectively) was carried out under the radiation of ultraviolet light or sunlight.

TABLE I

γ-KETO ACIDS (III)

R	Yield, %	Mp, °C Obsd	Mp, °C Lit.
C_3H_7	70	50–50.5	50,[a] 48.5–49.5[b]
C_5H_{11}	83	64–65	65–66,[c] 64–66[d]
C_6H_{13}	85	60–60.5	60,[e] 65–66,[f] 70.5[g]
C_8H_{17}	80	76	77–78[f]

[a] R. H. Wiley and J. R. Harrell, *J. Org. Chem.*, **25**, 903 (1961). [b] A. S. Perlin and C. B. Purves, *Can. J. Chem.*, **31**, 227 (1953). [c] J. Wotiz and E. S. Hudak, *J. Org. Chem.*, **19**, 1580 (1954). [d] F. L. Breusch and H. Keskin, *Arch. Biochem.*, **18**, 305 (1948); *Chem. Abstr.*, **43**, 3785[d] (1947). [e] See ref 9. [f] See ref 10. [g] See ref 11.

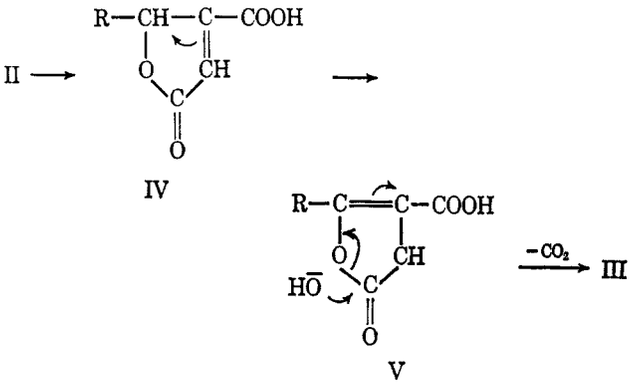
The structure of the reaction intermediates, which were separated at the treatment of II with an alkaline solution at room temperature for 10–30 min, has been assigned to aconic acids (IV)[3] which have carbonyl bands at 1740 cm^{-1} for lactone and at 1710 cm^{-1} for carboxylic acid. A series of aconic acids (IV) separated are shown in Table II. Treatment of the dibromo acids (II, R = C_5H_{11}, C_6H_{13}, and C_8H_{17}) with boiling water, as reported by Fittig, *et al.*,[2] on the acids (II, R = CH_3[2c] and *i*-C_4H_9[2b]), did not give the expected acids (IV).

Migration of the double bond on methyl ester of aconic acid (IV, R = C_3H_7) was encountered during distillation. Infrared spectra of the distillates showed characteristic absorption bands[4] due to the methyl ester of V (R = C_3H_7) at 1810 (lactone carbonyl), 1710 (conjugated ester carbonyl), and 1660 cm^{-1} (conjugated double bond). The nmr spectrum of the methyl ester of V (R = C_3H_7) showed the resonances of the methylene group (triplet, J = 6.5 cps) attached to γ-carbon atom centered at τ 7.5 and the methylene group (quartet, J = 2.0 cps) at the α position of the lactone ring centered at τ 6.9.

(3) Although aconic acid is described as a $\Delta^{\beta,\gamma}$-butenolide in earlier literature,[2] recent preparative and spectroscopic studies reveal that the structure should be $\Delta^{\alpha,\beta}$-butenolide. See N. R. Campbell and J. H. Hunt, *J. Chem. Soc.*, 1176 (1947); R. F. Rekker, P. J. Brombacher, H. Hamann, and W. Th. Nauta, *Rec. Trav. Chim.*, **73**, 410 (1954). The structure of IV (R = C_6H_{13}) is evidenced by the nmr spectrum, indicating that the resonances of the γ-methine (triplet) of the lactone ring centered at τ 5.1 and the α-methine (singlet) at τ 3.3 were each equivalent to one proton.

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1958, p. 186.

The mechanism of the formation of III involves an intermediate such as IV that may isomerize into enol-lactone V[5] which undergoes prompt fission of the lactone ring together with elimination of carbon dioxide in the alkaline medium.[6]



Experimental Section[7]

Preparation of dibromo acids and their conversion to γ-keto acids are exemplified by the following experiments. The yields and analyses of the new alkylidenesuccinic acids and the corresponding dibromo acids are listed in Tables III and IV, respectively.

2-Heptylidenesuccinic Acid (I, R = C_6H_{13}).—3-Carbethoxy-3-decenoic acid, Stobbe half-ester (12 g, 0.05 mole), obtained by condensation of heptanal with diethyl succinate in the presence of potassum *t*-butoxide,[8] was hydrolyzed with 150 ml of 1 *N* aqueous alkaline solution at 80–90° for 6–8 hr. The alkaline solution, after cooling to room temperature, was acidified with dilute sulfuric acid. The crude product was filtered and washed with 10 ml of ether and then recrystallized from benzene to give 8.7 g (82%) of white crystalline material: mp 130–131°; infrared 1700 and 1685 cm^{-1} (carboxylic acid, C=O); λ_{max}^{EtOH} 216 mμ (ε 1200).

3-Carboxy-3,4-dibromodecanoic Acid (II, R = C_6H_{13}).—Bromination of 10.7 g (0.05 mole) of 2-heptylidenesuccinic acid (I, R = C_6H_{13}) was carried out in 10 ml of carbon tetrachloride under radiation of ultraviolet light or sunlight for 5–6 hr at room temperature with 12 g of bromine. When the absorption band at 1635 cm^{-1} (double bond) vanished, the bromide (II, R = C_6H_{13}) was collected and washed with *n*-hexane. Recrystallization from toluene gave 17.8 g (95%) of 3-carboxy-3,4-dibromodecanoic acid, white crystals, mp 142–142.5°.

γ-Ketodecanoic Acid (III, R = C_6H_{13}).—A mixture of 11.5 g (0.03 mole) of 3-carboxy-3,4-dibromodecanoic acid and 90 ml (0.09 mole) of 1 *N* sodium hydroxide solution was stirred for 1 hr at 80–90°. Upon cooling to room temperature, the alkaline solution was acidified with dilute sulfuric acid. The white precipitate was filtered and recrystallized from petroleum ether (bp 75–120°) giving 4.9 g (85%) of white needles, mp 60.5° (lit. mp 60°,[9] 65–66°,[10] 70.5°[11]). This γ-keto acid gave correct analyses for carbon and hydrogen. The infrared spectrum of this material was identical with that of an authentic sample. The acid III (R = C_6H_{13}) was converted into γ-methyldecanolactone,[1] by the action of methylmagnesium iodide, and was

(5) R. Fittig and A. Schmidt, *Ann.*, **256**, 108 (1890); R. Fittig and J. Kraencher, *ibid.*, **256**, 103 (1890).

(6) This assumption is supported by the behavior of naturally occurring protolichesteric acid that can be converted into the corresponding keto acid by boiling with aqueous alkaline solution: M. Asano and T. Kanematsu, *Chem. Ber.*, **65**, 1175 (1932).

(7) Microanalyses were performed by Miss Teruko Nisi and ultraviolet measurements by Miss Kae Kobayasi, both of our laboratory. All melting points and boiling points are uncorrected.

(8) W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 1 (1951).

(9) A. P. Meshcheryakov and L. V. Petrova, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 106 (1958); *Chem. Abstr.*, **52**, 11746e (1956).

(10) A. A. Ponomarev and M. D. Liapnova, *Zh. Obshch. Khim.*, **32**, 2535 (1962); *Chem. Abstr.*, **58**, 9067a (1962).

(11) I. Ernest and H. Jelinkova, *Collection Czech. Chem. Commun.*, **24**, 3341 (1959); *Chem. Abstr.*, **54**, 4375g (1958).

TABLE II
ACONIC ACIDS (IV)

R	Yield, %	Mp, °C	λ_{max}^{EtOH}, mμ (ε)	C, % Calcd	C, % Found	H, % Calcd	H, % Found
C_3H_7	70	124–125[a]	216 (10,600)	...	...	...	...
C_5H_{11}	73	133–133.5	217 (10,300)	60.59	60.52	7.12	7.07
C_6H_{13}	75	125–126	218 (10,300)	62.25	62.41	7.60	7.69
C_8H_{17}	70	129–130	216 (12,500)	64.98	64.92	8.39	8.35

[a] See ref 5.

TABLE III
ALKYLIDENESUCCINIC ACIDS (I)

R	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found
C_3H_7	70	157.5–158[a]	...	...	...	...
C_5H_{11}	75	141–142	59.98	59.97	8.05	7.88
C_6H_{13}	82	130–131	61.66	61.65	8.47	8.49
C_8H_{17}	70	129–130	64.43	64.46	9.15	9.06

[a] Lit.[5] mp 159°.

TABLE IV
3,4-DIBROMO-3-CARBOXYALKANOIC ACIDS (II)

R	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found
C_3H_7	70	170–170.5	28.98	29.19	3.95	3.70
C_5H_{11}	90	140–141	33.46	33.75	4.48	4.56
C_6H_{13}	95	142–142.5	35.29	35.39	4.85	4.78
C_8H_{17}	90	124.5–125	38.82	39.09	5.51	5.49

identified by its infrared spectra. A number of the γ-keto acids prepared in this way are shown in Table I.

γ-Hexylaconic Acid (IV, R = C_6H_{13}).—A mixture of 11.5 g (0.03 mole) of 3-carboxy-3,4-dibromodecanoic acid and 90 ml (0.09 mole) of 1 *N* potassium hydroxide solution was stirred for 10 min at 20°. The alkaline solution was acidified with dilute sulfuric acid. The white precipitate was collected and recrystallized from *n*-hexane to give 4.9 g (75%) of white needles: mp 125–126°; λ_{max}^{EtOH} 218 mμ (ε 10300); infrared 1738, 1710 (carbonyl), 1630 cm^{-1} (C=C) (see Table II).

The aconic acid IV (R = C_6H_{13}) was also converted into the corresponding γ-keto acid III (R = C_6H_{13}) by treatment with excess 1 *N* alkaline solution at 70–90° for 1 hr in quantitative yield.

Methyl γ-Hexylaconate.—The esterification was carried out with diazomethane. Rapid distillation gave a fraction boiling at 116° (3 mm): $n^{20}D$ 1.4600; infrared 1755 (lactone carbonyl), 1715 (ester carbonyl), 1655 cm^{-1} (double bond).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 64.07; H, 8.37.

Decomposition of Ethyl Diazoacetate by a π-Allylic Palladium Chloride Complex

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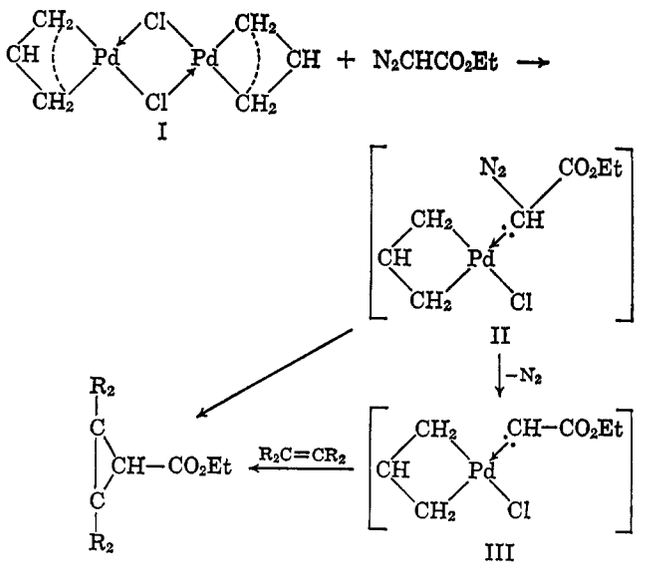
It is well known that diazo compounds are decomposed thermally, photochemically, and catalytically[1] with copper or copper salts. We have found that di-μ-chlorodi-π-allyldipalladium (I)[2] catalytically decomposes ethyl diazoacetate under very mild conditions. The products of this decomposition appear to arise from a carbene or related intermediate. A proposed mechanism is given in Scheme I. This mechanism is supported by the fact that bridged palladium complexes (I) are split by nucleophiles,[3] and ethyl diazoacetate may act in this fashion to give II. The complex II may then lose nitrogen to form III or may react directly with ethyl diazoacetate or the solvent.

SCHEME I



The results of these studies are summarized in Table I. It is of interest to note that palladium complex catalysis employed in the decomposition of ethyl diazoacetate gives virtually all diethyl fumarate, whereas the copper catalysis gives mainly diethyl maleate.[4]

The complex I is an efficient catalyst for the reaction of 2-butyne and ethyl diazoacetate at 0–10° to give ethyl 1,2-dimethyl-1-cyclopropene-3-carboxylate (IV); copper or copper salts are effective only at higher temperatures (65–120°). (See Scheme II.)

The cyclopropene IV did not react further even in the presence of a 5 molar excess of ethyl diazoacetate with the palladium complex even at 75°. On the other hand, the use of copper in refluxing benzene catalyzes the reaction of the cyclopropene IV and ethyl diazoacetate, and a small amount of the new compound, diethyl 1,3-dimethylbicyclo[1.1.0]butane-2,4-dicarboxylate (V), and two isomers of diethyl 3,4-dimethylmuconate were obtained.

(1) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 108–156.

(2) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

(3) S. D. Robinson and B. L. Shaw, *ibid.*, 4807 (1963).

(4) Control experiments with the palladium complex or copper with diethyl maleate or fumarate in refluxing benzene for 1.5 hr showed no isomerization.