Reactions of Amines. XIII. The Oxidation of N-Acyl-N-arylhydroxylamines with Lead Tetraacetate[1,2]

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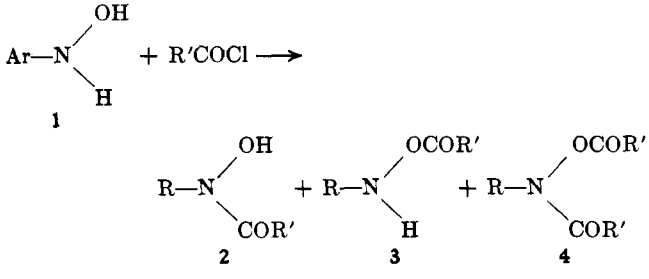
The reaction of lead tetraacetate with N-acyl-N-arylhydroxylamines produced the corresponding nitroso compounds. The reaction required less than 10 sec. at low temperatures and gave moderate to good yields of the nitroso derivatives.

The reactions of lead tetraacetate with hydroxyl groups (including *vic*-glycols and α-hydroxycarbonyl compounds), double bonds, and activated hydrogen atoms attached to carbon have been well documented.[3,4] Less well studied have been the reactions of this interesting reagent with organic nitrogen compounds. This communication is the second of a series[5] to be devoted to the reactions of the latter type and describes the extension of the well-known oxidative cleavage of α-hydroxycarbonyl compounds[6,7] to the N-acyl-N-arylhydroxylamines **2** (N-arylhydroxamic acids).

The procedure used for the preparation of **2** involved the partial acylation of the appropriate N-arylhydroxylamine **1** with acetyl or benzoyl chloride in aqueous or benzene–pyridine solution.[8] As was first noted by

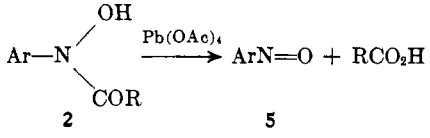


Bamberger,[9] in most experiments the acylation appeared to be complicated by the concomitant formation of the diacylated derivative **4** (and possibly the O-acylated arylhydroxylamine **3**). Fortunately, all of the N-acylated derivatives **2** were reasonably soluble in aqueous (28%) ammonium hydroxide[9] or, preferably, *cold*, 5–10% aqueous sodium hydroxide. This property provided a convenient method of separating **2** from **4** (and any **3**, if present), the latter being insoluble in base.

The N-benzoyl compounds were stable even when impure, whereas the N-acetyl compounds tended to decompose on storage unless carefully purified.

The infrared spectra of the various derivatives of **2**, which are recorded in Table I, correlate very well with the generalizations made previously.[5,10] Thus, the value for ν(C=O) (in chloroform) of **2b** was 1642 cm.$^{-1}$, which is very close to the value of 1646 cm.$^{-1}$ reported for α-acetylphenylhydrazine, the N-amino analog of **2b**, and well below that for acetanilide, 1686 cm.$^{-1}$. As in the instance of the N-amino compound, it seems probable that the low value for the ν(C=O) band is caused by hydrogen bonding. This interpretation is supported by the broadness of the ν(O—H) band at *ca.* 3300 cm.$^{-1}$.

Oxidation of N-benzoyl-N-phenylhydroxylamine (**2a**) proceeded rapidly and cleanly according to the following equation at temperatures as low as −60°. However,



a, Ar = C_6H_5; R = C_6H_5
b, Ar = C_6H_5; R = CH_3
c, Ar = *p*-$CH_3C_6H_4$; R = C_6H_5
d, Ar = *p*-ClC_6H_4; R = C_6H_5
e, Ar = *p*-ClC_6H_4; R = CH_3

at temperatures above *ca.* −10° and for reaction times greater than *ca.* 10 sec., secondary reactions became important and yields of nitrosobenzene (**5a**) were diminished. As is apparent from Table II, the most favorable conditions found involved use of either propionic acid or ethanol–acetic acid as solvent, reaction temperatures of −20° or below, and reaction times less than 10 sec. Use of ethanol–acetic acid as solvent had a second advantage in that, in the isolation of the nitroso compound by *rapid* steam distillation, the ethanol distilling with the steam and product appeared to dissolve traces of colored impurities apparently mechanically entrained in the steam and to give a more nearly pure product.

That the by-product of the oxidation was the corresponding acid was demonstrated by the isolation of approximately the expected quantity of benzoic acid from an oxidation of **2a**.

Other oxidizing agents have been reported to yield unspecified quantities of **5** and **2**.[9] Thus, the action of lead tetraacetate on **2** need not be unique. However, because of the rapidity of the reaction at low temperatures and high yields, it seems probable that the mechanism of this oxidation is similar to that for cleavage of α-hydroxycarbonyl compounds (and *vic*-glycols) by lead tetraacetate. Although all of the details of the latter mechanism have yet to be developed, the

(1) Paper XII: H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *J. Am. Chem. Soc.*, **85**, 3303 (1963).

(2) This work was supported in part by Public Health Service Research Grant CA-3090, from the National Cancer Institute.

(3) R. Criegee, *Angew. Chem.*, **53**, 321 (1940); **70**, 173 (1958).

(4) R. Criegee in "Newer Methods of Preparative Organic Chemistry," Vol. I, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1948, p. 16; Vol. II, 1963, p. 368.

(5) For the first see H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Am. Chem. Soc.*, **82**, 3977 (1960).

(6) E. Baer, *ibid.*, **62**, 1597 (1940); **64**, 1416 (1942).

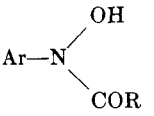
(7) E. Caspi, W. Schmid, and T. A. Wittstruck, *Tetrahedron*, **16**, 271 (1961).

(8) N-Benzoyl-N-phenylhydroxylamine (**2a**) is commercially available and is used as an analytical reagent: *cf.* D. E. Ryan [*Can. J. Chem.*, **38**, 2488 (1960)] for a leading reference to its preparation, properties, and use.

(9) E. Bamberger, *Chem. Ber.*, **52**, 1111 (1919).

(10) H. E. Baumgarten, R. Beckerbauer, and M. R. DeBrunner, *J. Org. Chem.*, **26**, 1539 (1961).

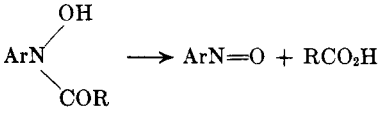
TABLE I
N-ACYL-N-ARYLHYDROXYLAMINES



Compd.	Ar	R	Yield,[a] %	M.p., °C.	ν(C=O), cm.⁻¹	ν(O—H),[b] cm.⁻¹
2a	C_6H_5	C_6H_5	60[c]	120–121	1632 (1628)	3200 (3300)
2b	C_6H_5	CH_3	33	67–67.5	1648 (1642)	3170 (3300)
2c	p-$CH_3C_6H_4$	C_6H_5	55	109–110	1643 (1623)	3130 (3300)
2d	p-ClC_6H_4	C_6H_5	40	156–157[d]	1620 (1631)	3180 (3280)
2e	p-ClC_6H_4	CH_3	60	113	1650 (1650)	3170 (3295)
2f	C_6H_{11}	C_6H_5	46	155–156	1615 (1616)	3140 (3290)

[a] Based on N-arylhydroxylamine. [b] Determined with a Model 21, Perkin-Elmer spectrophotometer using KBr pellets. All bands were very broad. Values in parentheses were for chloroform solutions. [c] Over-all from nitrobenzene. [d] With decomposition.

TABLE II
PREPARATION OF NITROSO COMPOUNDS



Compd.	Ar	R	Solvent	Temp., °C.	Time, sec.	Yield of ArN=O,[a] %
2a	C_6H_5	C_6H_5	HOAc	30	900	31
			HOAc	30	180	42
			EtOH	30	120	40
			HOAc[b]	14	120	56
			$EtCO_2H$	−20	10	58[c]
			HOAc–EtOH	−30	20	76
			HOAc–EtOH	−20	10	80
			HOAc–EtOH[d]	−20	15	59[c]
			$EtCO_2H$–EtOH	−20	10	71
2b	C_6H_5	CH_3	EtOH[e]	−40	30	53
			$EtCO_2H$	−10	20	68
			EtOH–HOAc	−20	15	64[c]
2c	p-$CH_3C_6H_4$	C_6H_5	$EtCO_2H$	−20	120	46
			EtOH–HOAc	−40	10	50
2d	p-ClC_6H_4	C_6H_5	EtOH	0	600	20
			EtOH	0	300	25
			$EtCO_2H$	−20	120	42
			EtOH–HOAc	−20	10	83
2e	p-ClC_6H_4	CH_3	$EtCO_2H$	−15	120	54
			$EtCO_2H$	−15	20	84
			EtOH–HOAc	−20	10	71

[a] The yields given here were obtained with lead tetraacetate containing about 7% acetic acid. Using the dry, powdered lead tetraacetate now available, the solution must be precooled to −40° or lower to obtain comparable yields. [b] Sodium acetate added, 5 g. [c] Color changes indicated time longer than optimum. [d] Starting material was used, 15 g. [e] Water added, 1 ml.

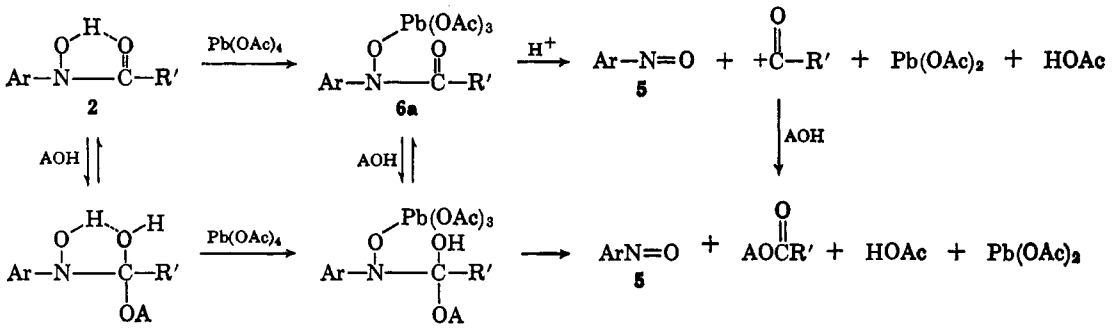
broad outlines of the most reasonable possibilities appear to be fairly well understood.[6,7,11] Thus, one fairly reasonable mechanism for the present oxidation is shown in outline form in the sequence **2** → **6** → **5**. On the basis of Baer's[6] results the route through **6b** would appear to be preferred. The more detailed steps of this mechanism may be inferred from the references cited.[6,7,11]

Good yields of nitroso compounds **5** (Table II) were obtained from the oxidation of several other N-acyl-N-arylhydroxylamines (**2b–2e**). In all instances the most favorable reaction conditions included short reaction times at sub-zero temperatures.

In a limited series of experiments the reaction of N-benzoylcyclohexylhydroxylamine with lead tetraacetate gave neither nitrosocyclohexane dimer nor cyclohexanone oxime (although pale green solutions were obtained). Inasmuch as an exhaustive study of the effects of varying reaction conditions was not carried out, these results must be regarded as very tentative.

At present the principal limitation on the practical use of this reaction is the moderate yields encountered in the preparation of some derivatives of **2**. However, **2a** is a commercially available reagent used in analytical chemistry[8] and is said to have a shelf-life in excess of 2 years (which is quite long compared with the short shelf-lives of nitrosobenzene and phenylhydroxylamine). Thus, the procedure described here would appear to afford a convenient, rapid preparation of small quantities of nitrosobenzene.

(11) For relevant discussion not specifically directed toward α-hydroxycarbonyl compounds, see (a) E. J. Moriconi, W. F. O'Connor, E. A. Kenneally, and F. T. Wallenberger, *J. Am. Chem. Soc.*, **82**, 3122 (1960); (b) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).



2 6a 5 6b 5

AOH = H_2O, HOAc, EtOH, etc.

Experimental[12]

N-Benzoylphenylhydroxylamine (2a).—The aqueous solution of phenylhydroxylamine resulting from the reduction of 50 g. (0.41 mole) of nitrobenzene by Kamm's[13] procedure (after removal and washing of the zinc oxide) was diluted to 1400 ml. and was treated with 45 g. (0.32 mole) of benzoyl chloride and 30 g. of sodium bicarbonate as described by Bamberger.[9] The monobenzoylated product was isolated by extraction of the reaction mixture with aqueous ammonia (28%) as described by Bamberger,[9] yielding 41 g. (60%) of N-benzoylhydroxylamine, m.p. 120–121° (lit.[14] m.p. 120–121°). The product was recrystallized, if necessary, from ethanol–water.

In later runs ice-cold 5% aqueous sodium hydroxide was substituted for the aqueous ammonia. This solution required less acid for neutralization and (especially for *para*-substituted derivatives) provided complete separation in one or, at the most, two extractions. When the solutions were kept cold, no appreciable hydrolysis of the acylated arylhydroxylamines was observed.

N-Acetylphenylhydroxylamine (2b).—To a solution of 15 g. (0.137 mole) of phenylhydroxylamine[13] in 70 ml. of benzene and 15 ml. of pyridine cooled to 0°, 11.6 g. (0.148 mole) of acetyl chloride was added dropwise with vigorous stirring. The ice bath was removed and the stirring was continued for an additional 2 hr. The resulting mixture was washed with ice-cold 3 *M* sulfuric acid, and the organic layer was extracted with aqueous ammonia (28%). Neutralization of the ammoniacal solution, followed by saturation of the solution with salt, produced a white, powdery product. Recrystallization from benzene and petroleum ether (b.p. 30–60°) gave 6.9 g. (33%) of N-acetylphenylhydroxylamine, m.p. 66.5–67.5° (lit.[15] m.p. 67–68°).

Anal. Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27; O, 21.17. Found: C, 63.39; H, 5.89; N, 9.21; O, 21.14.

N-Benzoyl-*p*-chlorophenylhydroxylamine (2d). A.—*p*-Chlorophenylhydroxylamine was prepared by a procedure based on Zinin's method.[16,17] A solution of 30 g. (0.19 mole) of *p*-chloronitrobenzene in 300 ml. of ethanol was cooled to 0–5° and saturated alternately with ammonia followed by hydrogen sulfide until the solution was filled with orange crystals of ammonium bisulfide. After the mixture had stood overnight, 200 ml. of ether was added to precipitate the ammonium polysulfide, which was removed by filtration and washed with ether. The resulting alcohol–ether solution was washed with water and evaporated under vacuum. The yellow, crystalline residue was triturated with benzene and diluted with petroleum ether. The solid was collected by filtration and recrystallized from benzene–petroleum ether, giving 19 g. (70%) of *p*-chlorophenylhydroxylamine, m.p. 87–88° (lit.[18] m.p. 87–88°). This procedure had the advantage of yielding a dry product, ready for acylation.

B.—Equally good results were obtained in a shorter time using Utzinger's[19,20] method on a 0.38-mole scale. The procedure as given[19,20] was followed. However, it was found desirable to add 6–8 ml. of the saturated ammonium chloride and then wait for the reaction to start and the mixture to begin to boil before further addition of the ammonium chloride was made. Otherwise the reaction was very difficult to control. The yield was 83% of *p*-chlorophenylhydroxylamine, m.p. 86–87°.

The 19 g. (0.132 mole) of *p*-chlorophenylhydroxylamine was dissolved in a mixture of 125 ml. of benzene and 30 ml. of pyridine; the mixture was cooled to 0–5° and 19.2 g. (0.137 mole) of benzoyl chloride diluted with 40 ml. of benzene was added dropwise with stirring. Upon completion of the addition, the ice bath was removed and the stirring was allowed to continue for an additional 2 hr., during which time the reactants warmed to room temperature. Dilute (3 *M*) sulfuric acid was added followed by ice to produce an aqueous layer of about 100 ml. Part of the product precipitated and was collected by filtration. The remainder was extracted from the benzene layer with aqueous ammonia. The ammoniacal solution was cooled in ice and neutralized with 3 *M* sulfuric acid. The combined white, powdery product was dried over phosphorus pentoxide, giving 13 g. (40%, 28% over-all) of N-benzoyl-*p*-chlorophenylhydroxylamine, m.p. 157° dec. The product was recrystallized, if necessary, from ethanol–water.

Anal. Calcd. for $C_{13}H_{10}ClNO_2$: C, 63.10; H, 4.04; N, 5.66. Found: C, 62.64; H, 4.06; N, 5.72.

N-Acetyl-*p*-chlorophenylhydroxylamine (2e).—This compound was prepared by the procedure described for N-acetylphenylhydroxylamine. The yield of N-acetyl-*p*-chlorophenylhydroxylamine was 12.5 g. (60%), m.p. 113°. This compound appeared to be more stable than N-acetylphenylhydroxylamine.

Anal. Calcd. for $C_8H_8ClNO_2$: C, 51.77; H, 4.34; Cl, 19.09; N, 17.55; O, 17.24. Found: C, 51.87; H, 4.64; Cl, 19.25; N, 17.47; O, 16.92.

N-Benzoyl-*p*-tolylhydroxylamine (2c).—When this compound was prepared by a method similar to the procedure described for N-benzoylphenylhydroxylamine the yields were very low, apparently due to the poorer solubility of the *p*-methyl derivative in water. Recrystallization from ethanol yielded 3–4 g. (6–8%) of N-benzoyl-*p*-tolylhydroxylamine, m.p. 109–110°.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.66; H, 5.76; N, 6.10.

The best yields were obtained on a 0.2–0.4-mole scale from a combination of Zinin's or Utzinger's method for the reduction of the nitro compound, which gave 68 and 77% yields, respectively, of *p*-tolylhydroxylamine, m.p. 92–94° (lit.[17,18c] m.p. 94°), followed by benzoylation in benzene–pyridine. The procedure used was similar to that described for N-benzoyl-*p*-chlorophenylhydroxylamine. The yield of N-benzoyl-*p*-tolylhydroxylamine was 55% (based on the hydroxylamine), m.p. 109–110°.

N-Benzoylcyclohexylhydroxylamine (2f).—The cyclohexylhydroxylamine was prepared by the general method described by Müller.[21] A solution of 19.6 g. (0.20 mole) of cyclohexanone and 13.9 g. (0.20 mole) of hydroxylamine hydrochloride in 200 ml. of water was hydrogenated at 50 p.s.i. pressure over platinum oxide. After about 2 hr., the catalyst was removed and the solution was neutralized with 2 *N* sodium hydroxide. The re-

(12) Melting points are corrected. Analyses were by Micro-Tech Laboratories, Skokie, Ill., and by A. Bernhardt, Mülheim (Ruhr), Germany.

(13) O. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 445.

(14) D. E. Ryan and G. D. Lutwick, *Can. J. Chem.*, **31**, 9 (1953).

(15) E. Bamberger, *Chem. Ber.*, **61**, 636 (1908).

(16) H. Zinin, *J. prakt. Chem.*, [1] **27**, 140 (1842).

(17) R. Willstätter and H. Kubli, *Chem. Ber.*, **41**, 1936 (1908).

(18) (a) E. Bamberger and M. Knecht, *ibid.*, **29**, 863 (1896); (b) O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, **78**, 3363 (1956); (c) Y. Ogata, M. Tsuchida, and Y. Takagi, *ibid.*, **79**, 3397 (1957).

(19) G. E. Utzinger, *Ann.*, **556**, 50 (1944).

(20) G. E. Utzinger and F. A. Regenass, *Helv. Chim. Acta*, **37**, 1885 (1954).

(21) E. Müller, D. Fries, and H. Metzger, *Chem. Ber.*, **88**, 1891 (1955).

sulting white precipitate was collected to yield 14.6 g. of crude cyclohexylhydroxylamine, m.p. 136–139°.

To a mixture of 20 g. of the crude product in 400 ml. of water and 50 ml. of benzene, 24 g. of benzoyl chloride was added dropwise while 25 g. of solid sodium bicarbonate was added in small portions to neutralize the hydrochloric acid formed. After 2 hr., 50 ml. of ether was added to assist in layer separation, and the aqueous layer was separated and discarded. The benzene layer was extracted with cold 3 *M* sodium hydroxide. Neutralization of the aqueous layer with 3 *M* sulfuric acid and collection and recrystallization of the solid from ethanol–water gave 18.1 g. (46%) of N-benzoylcyclohexylhydroxylamine, m.p. 155–156°.

Anal. Calcd. for $C_9H_9NO_2$: C, 63.56; H, 6.00; N, 9.27; O, 21.17. Found: C, 63.39; H, 5.89; N, 9.21; O, 21.14.

Oxidation Procedure.—The procedures for all of the oxidations cited in Table II were essentially the same except for the variations noted in the table. The procedure is illustrated by the oxidation of N-benzoylphenylhydroxylamine (**2a**).

A solution of 5.0 g. (0.023 mole) of N-benzoylphenylhydroxylamine (N-phenylbenzohydroxamic acid) in 100 ml. of a 1:1 solution of acetic acid–ethanol was cooled to −20°. While this solution was stirred rapidly, 11.5 g. (0.024 mole, based on 94% purity) of lead tetraacetate (Arapahoe Chemical) was added in one portion. In less than 10 sec. (and certainly no more than 15 sec.), when the bright green color which first appeared just *began* to darken, toward tan or brown, 100 ml. of water was added to decompose any unconsumed lead tetraacetate and the then brown to black mixture was steam distilled *as rapidly as possible*, the distillate being collected in a flask filled with ice. The distillate was filtered and the product was pressed dry between filter papers. Generally (because of the alcohol present) no further purification was required; however, the product could be recrystallized from alcohol–water. The yield of nitrosobenzene was 1.4–2.0 g. (56–80%).

The yield was dependent not only on the reaction time (times above 20 sec. often led to a loss of one-third or more of the possible yield) but also on the time required for steam distillation. When steam distillation was completed in 3 min., the yield was 73–80%; in 5 min., the yield was 56–65%.

When the reaction was allowed to proceed too long, the reaction mixture turned deep black. The only steam volatile product was the nitroso compound, albeit in greatly reduced yields. Presumably, the nitroso compounds were attacked by the lead tetraacetate, although more slowly than the N-acyl-N-arylhydroxylamines. The nature of these secondary oxidation products was not determined.

Propionic acid (100 ml.) could be substituted for the 1:1 acetic acid–ethanol; however, the latter not only facilitated the steam distillation (alleviating any tendency toward blockage of the condenser) but also yielded a more nearly pure product (dissolving some of the impurities present in the distillate).

Optimum conditions for large-scale runs were not determined. One run, three times the indicated size, gave a 59% yield, but the mixing time and the time required for steam distillation were obviously too long.

Some recent samples of lead tetraacetate, as received, appeared to give lower yields than older samples. Inasmuch as these samples contained less acetic acid (which tends to stabilize the reagent and lower its activity), these samples were moistened with acetic acid (7 ml./100 g. of lead tetraacetate) and allowed to stand overnight before use. In addition the temperature was brought to −40° before addition of the lead tetraacetate.

The identities of the nitroso compounds were confirmed by comparison of their infrared spectra in potassium bromide disks (*i.e.*, as the nitroso dimers) and of their melting points with those reported by Lüttke[22] (Table III).

TABLE III
PROPERTIES OF NITROSO COMPOUNDS

Compd.	D.M.S. card no.[a]	M.p., °C.	Lit.[a] m.p., °C.
Nitrosobenzene	5363	66–68	68
p-Nitrosotoluene	5365	46–48	47.5–48
p-Nitrosochlorobenzene	5368	86–88	89.5

[a] Reference 22.

Isolation of Benzoic Acid.—Benzoic acid was isolated from the aqueous residue left in still pot from an oxidation of N-benzoylphenylhydroxylamine by extraction with ether. The ether was extracted with 3 *M* sodium hydroxide and the aqueous solution was neutralized with 3 *M* sulfuric acid. The benzoic acid which precipitated melted at 120–121° and had an infrared spectrum identical with that of an authentic sample. Yields of 2.1–2.9 g. (60–85%) were obtained.

(22) W. Lüttke, Documentation of Molecular Spectroscopy, cards no. 5363, 5365, and 5368, Butterworths and Co. (Publishers) Ltd., London.

Stereochemistry of the Decarboxylation of Some 1,1,2-Cycloalkanetricarboxylic Acids[1]

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The stereochemistry of the decarboxylation of the 1,1,2-tricarboxylic acids of the three-, four-, five-, and six-membered carbocyclic rings has been determined in collidine, 5 *N* HCl, and without a solvent. In collidine only the cyclopropyl compound yields any *trans* isomer of the 1,2-dicarboxylic acid; all the others yield exclusively the *cis* isomers. In 5 *N* HCl all four of the acids give mainly *trans* isomers. Decarboxylation without solvent gives largely *cis* isomers. These results are rationalized in terms of steric control of the process depending on the bulk of the proton donor in its approach to the enol intermediate, but modified somewhat by ring strain.

The decarboxylation of α-substituted 1,1-dicarboxylic acids (substituted malonic acids) has been used synthetically for many years, but relatively little attention has been paid to mechanism or stereochemistry. The subject of stereochemistry arose in this laboratory when it was noted that the ratio of *cis*- to *trans*-1,2-cyclobutanedicarboxylic acid varied with conditions of decarboxylation of 1,1,2-cyclobutanetricarboxylic acid. It was deemed of interest to pursue the study of decarboxylation stereochemistry through the three-, four-, five-, and six-membered rings, and note the effect of conditions on the geometry of the product. It was discovered at once that the several reports in the literature[2] on the subject were contra-

(1) Abstracted from the Ph.D. Thesis of D. J. J. Lennon, University of Rhode Island, 1961. Presented in part before the Division of Organic Chemistry, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

(2) (a) E. Buchner, *Ann.*, **284**, 197 (1895); (b) W. H. Perkin, *J. Chem. Soc.*, **65**, 572 (1894); (c) E. Buchman, *J. Am. Chem. Soc.*, **64**, 2696 (1942); (d) A. Kotz and P. Spiess, *J. prakt. Chem.*, [2] **64**, 394 (1901); (e) R. Kuhn and A. Wasserman, *Helv. Chim. Acta*, **11**, 50, 70, 79, 600 (1928); (f) A. Wasserman, *ibid.*, **13**, 207, 223 (1930); (g) R. C. Fuson, C. L. Fleming, P. F. Warfield, and D. E. Wolf, *J. Org. Chem.*, **10**, 121 (1945).