incurred by accidental exposure of the samples to air during the processing, for a $CO_3^=-CO_2$ exchange does occur on moist carbonate. It is significant, furthermore, that the sodium formate exhibited no activity. The experiment was repeated using labeled formate and inactive carbonate, and in this series no activity was transferred to the carbonate.

Results and Discussion

The yield of peroxide varies considerably with the additive concentration and it seemed appropriate to investigate the reaction over a wide range of concentrations. The results are shown in Tables II and III.

TABLE II

PHOTOLYSIS PRODUCTS IN THE SODIUM FORMATE SUSPENSION

NaO_2CH, moles/l.	Yield of peroxide, moles × 10^5	Yield of CO_2,[a] moles × 10^5	Formate oxidized/peroxide formed
6.0×10^{-1}	7.1	7.2	1.0
	6.5	7.0	1.1
1.5×10^{-1}	10.1	10.2	1.0
	6.6	6.1	0.9
1.23×10^{-2}	5.7	6.0	1.1
	5.9	6.0	1.0
1.23×10^{-3}	3.8	4.0	1.1
	3.8	4.1	1.1
	3.8	4.2	1.1
1.23×10^{-4}	1.1	0.9	0.8
	1.1	1.0	0.9
	1.0	1.0	1.0
1.23×10^{-5}	0.8	0.3	0.4
	0.8	0.1	0.1
	0.8	0.1	0.1

[a] Based on the specific activity of sodium formate = 43.8 μc./mole.

TABLE III

PHOTOLYSIS PRODUCTS IN THE POTASSIUM OXALATE SUSPENSION

$K_2C_2O_4$, moles/l.	Yield of peroxide, moles × 10^5	Yield of CO_2,[a] moles × 10^5	Oxalate oxidized[b]/peroxide formed
1.02×10^{-1}	6.2	20.0	1.6
	5.8	20.0	1.7
1.02×10^{-2}	3.2	13.0	2.0
	4.0	12.4	1.5
	4.5	10.2	1.2
1.02×10^{-3}	2.3	5.2	1.1
	2.3	5.8	1.3
	2.4	5.4	1.1
1.02×10^{-4}	0.75	1.4	0.9
	1.0	1.8	0.9
	0.8	1.6	1.0
1.02×10^{-5}	0.5	0.2	0.2
	0.6	0.2	0.2

[a] Based on specific activity of potassium oxalate = 789 μc./mole. [b] Each mole of oxalate yields two moles of CO_2.

The production of $C^{14}O_2$ confirmed the oxidation of the formate and oxalate during the synthesis of hydrogen peroxide. The mole-for-mole oxidation (column 4), furthermore, proves clearly that the yield of peroxide is dependent on the reductive properties of these compounds. The possibility that the additive may be oxidized only in a subsequent reaction with the peroxide seems very remote in view of the exact stoichiometric relationship at various yields of peroxide, particularly in the formate case. The mole ratio of one with formate persists, furthermore, from 0 to 30°, a condition very unlikely to exist if independent thermal (oxidation) and photochemical (formation) reactions were involved.

The stoichiometric relationship with both additives falls considerably below unity at the lowest concentration (10^{-5} *M*) which might indicate a limited yield of H_2O_2 without additive participation. Indeed, approximately the same peroxide yield is obtained in "additive-free" suspensions. It seems more probable, however, that oxidizable impurities account for the small non-additive yields and for the excess in the dilute additive solutions. The presence of impurity is indicated by the observation that this zinc oxide darkens if heated *in vacuo*, but not if preheated in an oxygen atmosphere. Also, commercial oxygen supplies are known to contain some hydrocarbon impurities.[12] The reaction has not been studied under conditions which meticulously avoid contamination from sources such as the foregoing. Accordingly, no definite conclusion can be reached concerning the dilute and the non-additive systems, and no previous observation can be regarded as reliable proof that peroxide can be produced in the absence of oxidizable matter.

At the higher concentrations of oxalate the mole ratios indicate excessive oxidation of the oxalate, but this is not unexpected in view of the photosensitive properties of oxalates. It was found, furthermore, that the light can induce a reaction between the peroxide and additive resulting in the increased mole ratio.

A third organic additive, ethanol, was studied as a sort of prototype of the compounds with several oxidation products. The tracer technique, however, did not prove very useful in this case. Ethanol is apparently not oxidized to CO_2; indeed, no oxidation product was definitely established by radioactivity techniques. In separate procedures the attempted recovery of (a) acetaldehyde by precipitation with 2,4-dinitrophenylhydrazine, and (b) acetic acid by evaporation of the filtered reaction mixture (rendered alkaline) resulted in samples with negligible or unreproducible activities. It is not legitimate, therefore, to state categorically that all additives participate as do the oxalate and formate, even though all other indications[7,8] including the foregoing studies suggest that they do.

Acknowledgment.—The authors wish to thank Miss Linda Simpson for making the radioactivity measurements reported in this paper.

[12] L. A. Wooten and W. A. Guldner, *Anal. Chem.*, **14**, 835 (1942).

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2-Pyrones. VII. 2-Pyridones from 2-Pyrones

BY RICHARD H. WILEY, L. H. KNABESCHUH, A. L. DUCKWALL AND N. R. SMITH

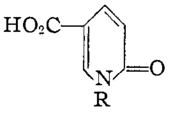
RECEIVED JULY 27, 1953

In a previous paper[1] we presented data on the preparation and properties of some 5-carboxy-2-

[1] R. H. Wiley, N. R. Smith and L. H. Knabeschuh, THIS JOURNAL, **75**, 4482 (1953).

pyridones prepared from phenylethylamine and its derivatives with methyl coumalate. 2-Pyridones of this type not having been previously characterized, we have continued these studies and wish to report here the preparation and properties of several previously uncharacterized compounds.

5-Carboxy-2-pyridones (I) have been prepared in 14–81% yield from methyl coumalate and benzylamine, *p*-methoxybenzylamine, α-methylbenzylamine[2] and *p*-methoxyphenylethylamine. These compounds can be titrated as monobasic acids and have melting points between 180 and 208°. No characterizable products were obtained in similar reactions with either tyramine or *p*-hydroxybenzedrine.[3]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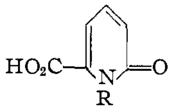
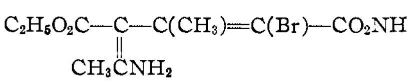
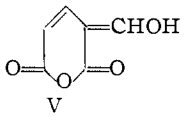
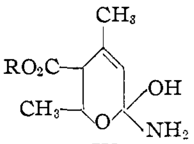
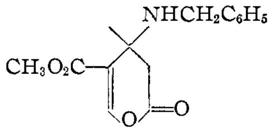

II

The reaction of methyl coumalate with benzylamine differs from that with other amines in that these reactants deposit crystals on standing in methanol solution. The product is obtained in 52% yield. After recrystallization from water the product melts at 108–109° and gives analyses in accord with a structure in which the amine and ester have combined without loss of water or methanol. This fact coupled with its ultraviolet absorption characteristics, which are distinct from those of other 2-pyridones, eliminates the pyridone structure. Since the product is convertible to the pyridone only in low yield (*ca.* 20%), any structure related to the pyridone in a direct way seems unlikely. Addition compounds have been obtained previously from ammonia and isodehydroacetic acid derivatives and formulated variously as open chain derivatives[4] (III) and cyclic carbonyl addition products[5–7] IV. Apparently, this is the first time an addition product has been obtained from a coumalic acid derivative although it has been reported that ammonia converts ethyl coumalate to an amide of "isocoumalinic" acid (V).[8] Analogs of these (III, IV and V) seem rather unlikely as possible structures for these products and we would like to suggest a further possibility—that of a 1,4- (or 1,6-) addition product VI in which the amine adds to the conjugated unsaturation of the lactone ring. Conversion of VI to the pyridone perhaps takes place by dissociation to the amine and pyrone.


$$C_2H_5O_2C{-}\underset{\underset{\textstyle CH_3CNH_2}{\|}}{C}{-}C(CH_3){=}C(Br){-}CO_2NH_4$$
III


V


IV


VI

6-Carboxy-2-pyridones (II) have been prepared from 2-pyrone-6-carboxylic acid with phenylethylamine and its 3,4-dimethoxy derivative. The reaction was run in glacial acetic acid and gave 30–37% yield of the pyridone. The properties of these compounds are recorded in Table I.

TABLE I

N-ALKARYL-5 AND 6-CARBOXY-2-PYRIDONES

Compound	M.p., °C.	Yield, %	N, Anal. Calcd.	N, Anal. Found	Neut. equiv. Calcd.	Neut. equiv. Found
R of formula I						
$C_6H_5CH_2$	206–208	45	6.11	5.95	229	226
4-$CH_3OC_6H_4CH_2$	198–199	81	5.41	5.40	259	254
$C_6H_5CH(CH_3)$	192–194	18	5.76	5.60	243	232
4-$CH_3OC_6H_4CH_2CH_2$	180–181	14	5.13	4.94	273	256
R of formula II						
$C_6H_5CH_2CH_2$	192–193	37	5.76	5.58	243	241
3,4-$(CH_3O)_2C_6H_3CH_2CH_2$	218	30	4.62	4.42	303	301

The ultraviolet absorption curves of seven N-alkaryl-5-carboxy-2-pyridones obtained in the present and previous studies[1] show an unmistakable similarity. There is a strong absorption maximum at 260 mμ and a clearly defined, yet lower, maximum at 295–306 mμ. There is evidence of a third maximum at about 220 mμ which is shifted to 225–230 mμ in the methoxy compounds. The compound VI shows a strong absorption band at 326 mμ with a shoulder extending from 285–295 mμ. The curves for the N-alkaryl-6-carboxy-2-pyridones are characterized by maxima at 315 and 230 mμ with an additional maximum at 280 mμ in the curve for the dimethoxy derivative.

None of the 5-carboxy-2-pyridones described in this report has been successfully cyclized to quinolizinium salts or converted to pyridinium salts by techniques previously described.[1] This indicates that activation in the benzene ring is a requirement for successful cyclization to quinolizinium salts.

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Experimental[9]

The methyl coumalate used in the following experiments was prepared from coumalyl chloride and methanol. The 2-pyrone-6-carboxylic acid was prepared as previously described.[10] The 5- and 6-carboxy-2-pyridones listed in Table I were prepared by the following procedures described in detail for a typical example of each.

N-(*p*-Methoxybenzyl)-5-carboxy-2-pyridone (I, R = *p*-$CH_3OC_6H_5CH_2$).—Three grams (0.019 mole) of methyl coumalate in 15 ml. of methanol was added to a solution of 8.0 g. (0.058 mole) of *p*-methoxybenzylamine in 15 ml. of methanol with cooling under a tap. The flask was fitted with a calcium oxide drying tube and allowed to stand at room temperature for 8 days. To the mixture was added 6 g. of sodium hydroxide in 15 ml. of water. It was refluxed on a steam-bath for 20 minutes, cooled and acidified with dilute hydrochloric acid, to precipitate 4.42 g. of crude product. Some of the pyridones are water soluble and were ether extracted in a continuous extractor at this point. The crude product was dissolved in 5% sodium bicarbonate, warmed, treated with Norit and reprecipitated with dilute

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[2] The authors are indebted to Carbide and Carbon Chemicals Company for supplying samples of this amine.

[3] The authors are indebted to Dr. Glenn E. Ullyot of Smith, Kline and French Laboratories for supplying samples of this amine.

[4] F. Feist, *Ber.*, **26**, 747 (1893).

[5] A. Hantzsch, *Ann.*, **222**, 9 (1883).

[6] R. Anschütz, P. Bendix and W. Kerp, *ibid.*, **259**, 148 (1890).

[7] W. Kerp, *ibid.*, **274**, 267 (1893).

[8] H. v. Pechmann, *Ber.*, **34**, 1406 (1901).

[9] Analyses by Micro-Tech Laboratories.

[10] B. Prager, *Ann.*, **338**, 360 (1904).

hydrochloric acid, yielding 4.0 g. (81% of the theoretical amount) of N-(*p*-methoxybenzyl)-5-carboxy-2-pyridone. This was recrystallized twice from an ethanol–water mixture and once from water to give white, needle-like crystals melting at 198–199°.

N-(β-Phenylethyl)-6-carboxy-2-pyridone.—One gram (0.0072 mole) of 6-carboxy-2-pyridone and 1.8 g. (0.015 mole) of β-phenylethylamine were dissolved in 50 ml. of glacial acetic acid and refluxed 50 hours. The solvent was removed under reduced pressure on a steam-bath and the residue treated with 150 ml. of 5% hydrochloric acid. The crude N-(β-phenylethyl)-6-carboxy-2-pyridone was purified by dissolving in 5% sodium bicarbonate and reprecipitating with acid. Recrystallization from 50% aqueous ethanol gave 0.65 g. (37%) of product, m.p. 192–193°.

Methyl Coumalate–Benzylamine Addition Product.—Six grams (0.038 mole) of methyl coumalate and 10 g. (0.093 mole) of benzylamine were dissolved in 40 ml. of methanol. After 1.5 hours at room temperature a precipitate began to form. After 15 hours this precipitate was collected, washed and dried to give 5.73 g. (52% of the theoretical amount) of the addition product (VI?). After recrystallization from water the product melts at 108–109°. The compound shows absorption maxima at 287 mμ (ε 4.18) and 326 mμ (ε 4.39). It is converted by alkali in 20% yield to N-benzyl-5-carboxy-2-pyridone identical with that obtained by the above procedure as determined by the method of mixed melting points.

Anal. Calcd. for $C_{14}H_{15}O_4N$: N, 5.36. Found: N, 5.30, 5.34.

Ultraviolet absorption measurements were made in alcohol solution with a Beckman DU spectrophotometer using 1-cm. quartz cells.

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Configuration of 3-Substituted 1-Chloropropenes

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RECEIVED AUGUST 10, 1953

The configuration of the 1,3-dichloropropenes remained ambiguous even though considerable work had been done in an attempt to establish the structure of the two isomeric forms by means of relative reactivities[3] or by means of physical data,[4] until Hatch and Perry[5] succeeded in chemically transforming each isomer into a compound whose configuration had been established previously. Later work[6] on relative reactivities substantiated the chemical work of Hatch and Perry.[5] A further aid in the establishment of structure of the 1,3-dichloropropenes was encountered in the preparation of compounds in the 1-naphthalene series to be used in plant-growth regulator investigations.[7]

When the 1-naphthylmagnesium bromide reacted with 1,3-dichloropropene, 3-(1-naphthyl)-1-chloro-1-propene was obtained as a product[8] but no mention was made of the possibility of *cis–trans* isomerism. Harris[9] pointed out that two isomers were obtained in this reaction, a white solid melting at 50° and a pale yellow liquid boiling at 155–160° (6–7 mm.). He concluded that he had the *cis*- and *trans*-isomers of 3-(1-naphthyl)-1-chloro-1-propene and, from dipole moment studies conducted by Lander and Svirbely,[10] tentatively assigned the following configurations; solid isomer *trans*, liquid isomer *cis*. However, he made no effort to start with *cis*-1,3-dichloropropene and correlate that product with the corresponding naphthyl product.

The work of Hatch and Perry[5] established the isomeric forms of 1,3-dichloropropene as follows: low boiling isomer I, *cis*-configuration; high boiling isomer II, *trans*-configuration. Starting with pure *cis*-1,3-dichloropropene (I) and converting it to the 3-(1-naphthyl)-1-chloro-1-propene by way of the Grignard reaction, we obtained a white solid III as a product, while the *trans*-isomer (II) gave a liquid product (IV). This seemed at variance with the work of Harris[9] for the assignment of configuration to the 3-(1-naphthyl)-1-chloro-1-propenes. For this reason, dipole moment measurements on all these isomeric compounds were repeated (Table I) and, although possibly not of a conclusive nature, they show a correlation of the *cis-trans*-1,3-dichloropropenes with the isomeric 3-(1-naphthyl)-1-chloro-1-propenes.

TABLE I

DIPOLE MOMENTS OF 1,3-DICHLOROPROPENE AND 3-(1-NAPHTHYL)-1-CHLORO-1-PROPENE ISOMERS

Compounds	Debye units			Configuration
1,3-Dichloropropene				
104° isomer (I)	1.92 (4a)	..	1.85[11]	*cis*
112° isomer (II)	1.73 (4a)	..	1.74[11]	*trans*
3-(1-Naphthyl)-1-chloro-1-propene				
Solid isomer (III)	..	1.27(9,10)	1.60[11]	*cis*
Liquid isomer (IV)	..	1.47(9,10)	1.39[11]	*trans*

The infrared spectra of these compounds (Fig. 1) also are interpreted to indicate that the solid isomer of 3-(1-naphthyl)-1-chloropropene is the *trans* form, at variance with the work of Harris.[9] To aid in the interpretations, the curves of *cis*- and *trans*-3-chloropropenoic acid are shown also. The configuration correlations applying to simple ethylenic groups did not seem applicable because of the effect of an adjacent halogen atom in all cases, and of the complexity from aromatic unsaturation in some. However, a band near 7.5 μ consistently was of prominent intensity in all the isomers assigned the *cis*-configuration, and this was either absent or very weak in all the remaining (*trans*) isomers. Because other nearby spectral patterns correspond to a recognizable extent in the respective isomers,

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[1] National Bureau of Standards, Washington, D. C.

[2] Part of a Thesis presented by H. M. Doukas to Georgetown University, Washington, D. C., in partial fulfillment of the requirements for the degree of M.S.

[3] (a) L. F. Hatch and G. B. Roberts, THIS JOURNAL, **68**, 1196 (1946); (b) L. J. Andrews and R. E. Kepner, *ibid.*, **69**, 2230 (1947); (c) L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).

[4] (a) H. A. Smith and W. H. King, *ibid.*, **70**, 3528 (1948); (b) R. A. Oriani and C. P. Smyth, *J. Chem. Phys.*, **16**, 930 (1948); (c) A. Kirrmann, *Bull. soc. chim.*, **6**, 841 (1939); (d) W. West and M. Farnsworth, *Trans. Faraday Soc.*, **27**, 145 (1931).

[5] L. F. Hatch and R. H. Perry, Jr., THIS JOURNAL, **71**, 3262 (1949).

[6] (a) L. F. Hatch, A. N. Brown and H. P. Bailey, *ibid.*, **72**, 3198 (1950); (b) H. Pourrat and R. Schmitz, *Bull. soc. chim.*, 505 (1952).

[7] H. M. Doukas, W. C. Wolfe and T. D. Fontaine, *J. Org. Chem.*, in press.

[8] L. Bert and P. C. Dorier, *Bull. soc. chim.*, **37**, 1600 (1925); ;*ibid.* **39**, 1610 (1926).

[9] T. H. Harris, M.S. Thesis, George Washington University Washington, D. C., 1943.

[10] J. J. Lander and W. J. Svirbely, THIS JOURNAL, **66**, 235 (1944).

[11] Measurements were kindly made by Dr. A. Maryott, National Bureau of Standards, Washington, D. C.