The Convenient Preparation of Per-acids

BY FRANK P. GREENSPAN

The commercial availability of concentrated hydrogen peroxide (90% by weight) has now made possible a convenient, safe and rapid preparation of per-acids by simple interaction with aliphatic acids in the presence of 1% sulfuric acid as a catalyst. The procedure used is substantially the same as that employed by D'Ans and Frey[1,2] in their classical study of per-aliphatic acids.

Because of interest in the aliphatic per-acids for oxidation and hydroxylation reactions,[3] an investigation has been made of the comparative rate of per-acid formation with concentrated hydrogen peroxide (90%) and more dilute hydrogen peroxide (30%). With 90% hydrogen peroxide, it has been possible to prepare 46.0% peracetic acid solutions and 35.8% performic acid solutions, six- to seven-fold higher concentrations than obtained with previously used procedures employing 30% hydrogen peroxide. Results with 90% hydrogen peroxide check well with those obtained by D'Ans and Frey[1,2] using specially prepared 98–100% hydrogen peroxide.

Experimental

Peracetic Acid Formation with 90% Hydrogen Peroxide.—Ten grams of glacial acetic acid was added to specially cleaned volumetric flasks containing 0.11 ml. of concentrated sulfuric acid (1% concentration on total contents). The flask was immersed in a water-bath, agitated with an air stirrer, and maintained at 22–23°; 9.1 g. of 90% hydrogen peroxide was then added to the flask contents—the mole ratio of hydrogen peroxide to acetic acid being 1.5 to 1.0 as for succeeding experiments; 1 ml. aliquots were withdrawn at intervals, diluted to 100 ml. with ice cold water, and a 20-ml. aliquot titrated in the cold for hydrogen peroxide and peracetic acid content, using a modified procedure of D'Ans and Frey.[1,2] Results are plotted as the number of moles of peracid formed per mole aliphatic acid used *vs.* time, Curve 1. At the end of four hours, peracetic acid concentration is 44.4%, rising to a maximum of 46.0% within twelve to fifteen hours. D'Ans and Frey obtained an equilibrium within twelve to sixteen hours at a peracetic acid concentration of 51.5%.

Peracetic Acid Formation with 30% Hydrogen Peroxide.—Procedure was same as above using 28.8 g. of 30% hydrogen peroxide and 0.4 g. of sulfuric acid, Curve 2. Maximum peracetic acid concentration is 8.6% reached in eighty to ninety hours.

Performic Acid Formation with 90% Hydrogen Peroxide.—The procedure is same as for peracetic acid: 23.0 g. of formic acid (98–100%) reacted with 28.4 g. of 90% hydrogen peroxide in the presence of 1% sulfuric acid, Curve 3. Maximum performic acid concentration is 35.8% reached within thirty minutes compared to that of 48% reported by D'Ans and Frey in two hours.

Performic Acid Formation with 30% Hydrogen Peroxide.—The procedure is same as above using 9.2 g. of formic acid and 33.7 g. of 30% hydrogen peroxide in the presence of 1% sulfuric acid, Curve 4. Maximum performic acid concentration is 4.7% reached within two hours.

Stability and Storage.—Peracetic acid prepared from 90% hydrogen peroxide shows surprisingly good storage stability—75% of the peracid remaining after forty-nine days at room temperature for a typical unstabilized preparation, with still greater stabilities being shown by specially stabilized solutions (a sample containing 100 pts. per million of sodium pyrophosphate when tested after forty-nine days showed 94% of the original peracetic acid remaining). Performic acid is less stable, gassing being noticeable after a few hours of standing, and the effective concentration showing a definite decline in two hours. Decomposition of the peracids is exothermic. It is therefore advisable to maintain peracetic acid during formation and storage below 30°.

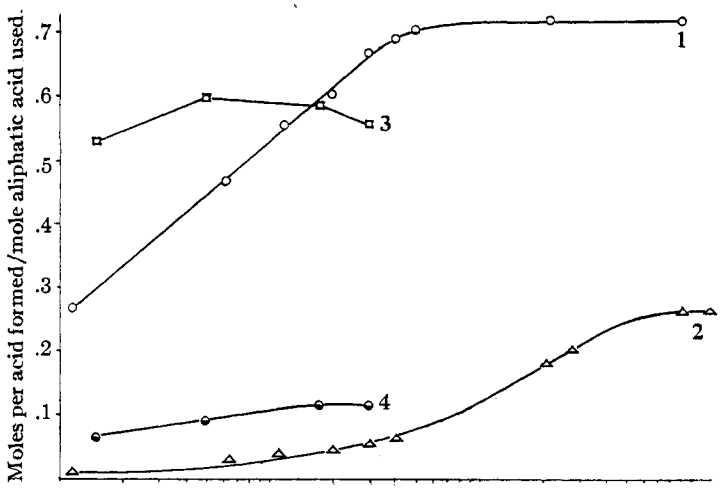


Fig. 1.—Curve 1, peracetic formation with 90% hydrogen peroxide; curve 2, peracetic formation with 30% hydrogen peroxide; curve 3, performic formation with 90% hydrogen peroxide (showing some decomposition); curve 4, performic formation with 30% hydrogen peroxide.

Acknowledgment.—The author wishes to thank Patricia Hogan and A. June Menge for aid in phases of the analytical work.

CONTRIBUTION FROM THE
RESEARCH DEPARTMENT OF THE
BUFFALO ELECTRO-CHEMICAL CO., INC.
BUFFALO, N. Y. RECEIVED DECEMBER 26, 1945

(1) D'Ans and Frey, *Ber.*, **45**, 1845 (1912).

(2) d'Ans and Frey, *Z. anorg. Chem.*, **84**, 145–164 (1913).

(3) Swern, Billen, Findley and Scanlan, THIS JOURNAL, **62**, 2305 (1940).

β,β'-Dipyridyl Ketone

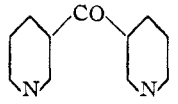
BY FRED LINSKER AND RALPH L. EVANS

Although no dipyridyl ketone has been reported to date, mention is made in the older literature[1] of a high-boiling base which was obtained in small amount in the dry distillation of calcium nicotinate. From 20 g. of the calcium salt was obtained 0.6 g. of a new base which was analyzed as the chloroplatinate and at that time believed to be a dipyridyl compound.

In our search for a suitable method of preparing β,β'-dipyridyl ketone we repeated Laiblin's experiment and confirmed his observations. A some-

(1) Laiblin, *Ann.*, **196**, 160 (1879)

what modified process, whereby the vapors of nicotinic acid were passed through a heated column of thorium dioxide, gave a comparable yield of the ketone. This was identified by analysis of the dipicrate. The same result was obtained when aluminum oxide was used in place of thorium dioxide.



Experimental

β,β′-Dipyridyl Ketone.—A Pyrex tube, 25 inches long, closed at one end, was charged with 20 g. of nicotinic acid, followed by 100 g. of thorium dioxide. The outlet was connected with a descending condenser and the receiving flask was immersed in an ice-bath. Nicotinic acid was slowly distilled through the thorium oxide layer which was kept at 300° during the process. The distillate was collected, and pyridine and water were boiled off at atmospheric pressure, leaving a dark residue which was extracted with ether. After the ether was evaporated, this extract yielded 0.4 g. of a viscous oil. The dipicrate, formed in alcoholic solution and recrystallized from alcohol, was in dark green plates; m. p. 135°.

Anal. Calcd. for $C_{11}H_8N_2O \cdot 2C_6H_3N_3O_7$: C, 42.99; H, 2.17. Found: C, 43.00; H, 2.02.

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RECEIVED JANUARY 31, 1946

The Relative Efficiency of Some Polymerization Inhibitors[1]

BY ROBERT L. FRANK AND CLARK E. ADAMS

Considerable losses often occur in the preparation of vinyl monomers due to their ease of polymerization, especially during distillation. The present comparison of inhibitors was undertaken to prevent such losses.

Equal weights (0.20 g.) of a number of compounds were added to 2.0-ml. samples of three monomers, styrene, 3,4-dichlorostyrene, and 5-ethyl-2-vinylpyridine, each freshly distilled. These monomers were chosen for their tendency toward ready polymerization. Each sample was sealed in a 10 × 110-mm. test-tube and allowed to stand in a refluxing water-bath. No effort was made to exclude oxygen from the tubes, but all were of the same size and had approximately the same air space above the monomer–inhibitor mixtures. The fluidity of the samples was periodically compared with the initial fluidity by means of the flow-times when the tubes were inverted. The heating time required to show a difference in flow-time is given in Table I as the "inhibition period." At the "total time of polymerization" the samples were too viscous to give a measurable flow time.

There appears to be no great variation in the order of inhibitory strength from one monomer to another. A good inhibitor for one monomer is likely to be good for another.

TABLE I

EFFECT OF INHIBITORS ON POLYMERIZATION

Inhibitor	Inhibition period, hr. S[a]	DCS[a]	VEP[a]	Total time of polymerization, hr. S[a]	DCS[a]	VEP[a]
Picric acid	299	39	<120	>490	130	>120
Trinitrobenzene	299	39		>490	82	
2,5-Dihydroxy-1,4 benzoquinone	154	32		442	82	
1,4-Naphthoquinone	81	22	120	251	66	>120
1,4-Benzoquinone	81	22	<120	130	66	>120
Chloranil	81	9		>490	34	
9,10-Phenanthraquinone	57	17		130	66	
t-Butylcatechol	34	9	12	154	17	72
4-Amino-1-naphthol	9	9	<120	130	17	>120
Hydroquinone	9	9	24	22	17	>120
Phenyl-β-naphthylamine	9	<9	12	17	9	72
Triphenyl phosphite	<9	<9		9	9	
Control	<9	<9	12	9	9	24

[a] S stands for styrene; DCS for 3,4-dichlorostyrene; VEP for 5-ethyl-2-vinylpyridine.

One fact that stands out in the present study is that phenyl-β-naphthylamine and *t*-butylcatechol, two widely used inhibitors, are among the poorest in inhibitory action at least for the monomers tried.

Picric acid and trinitrobenzene are now being used in this Laboratory with great success during distillation of a wide variety of monomers. Some question has arisen concerning the possible hazard from explosion of polynitro compounds, but the use of traces should involve no danger.[2] Picric acid should probably not be used, however, in metal containers.

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) *Cf.* Belyaev and Yuzefovich, *Compt. rend. acad. sci.* (URSS), **27**, 133 (1940); *C. A.*, **34**, 7607 (1940).

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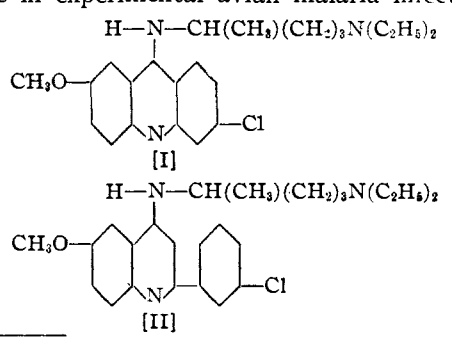
RECEIVED MARCH 11, 1946

Anils as "Open Models" of a Modified Atebrin

BY HENRY GILMAN AND SAMUEL P. MASSIE, JR.

In a recent study[1] concerned with some quinolines patterned as so-called open models of atebrin, [I], it was shown that a compound like 6-methoxy - 2-(3′ - chlorophenyl) - 4 - [(α - methyldiethylaminobutyl)-amino]-quinoline, [II], was active in experimental avian malaria infections.



(1) Gilman and Spatz, THIS JOURNAL, **66**, 621 (1944).