144. *Aliphatic Aldehydes in the Perkin Reaction.*

By Malcolm Crawford and W. T. Little.

Under the conditions of the Perkin reaction aliphatic aldehydes give diacetates and enol acetates. When temperatures are low enough to suppress these reactions and the acid component is activated the Perkin reaction does take place with aliphatic aldehydes, except for the higher members. Comparison of the rates of reaction of a number of aliphatic and aromatic aldehydes with acetic anhydride and sodium *p*-nitrophenylacetate by a competitive method indicates that the reluctance of aliphatic aldehydes to undergo the Perkin reaction is due to the slowness of the elimination stage. Higher aliphatic aldehydes are unreactive because of a " rule of six " effect.

THE failure, long known, of aliphatic aldehydes to undergo the Perkin reaction has never been satisfactorily explained. Many carbonyl reactions such as semicarbazone formation [1] and addition of the Grignard reagent [2] take place more readily with aliphatic than with aromatic aldehydes. The same might be expected to apply to the Perkin reaction: certainly addition of the anion from the acid component, acetic anhydride, should take place less readily with aromatic than aliphatic aldehydes because of mesomeric spreading of the positive charge from the carbonyl group into the aromatic ring: [3] the non-reactivity of aliphatic aldehydes in the Perkin and related reactions has been vaguely attributed to competing reactions, such as aldol formation, which involve the α-hydrogen atoms.[4] The standard bath-temperature for the Perkin reaction is 180°. Few of the commoner aliphatic aldehydes would remain as liquids in the reaction flask at this temperature. Experiments in sealed tubes with pentanal,[5] heptanal,[5] and other aldehydes [6] have afforded minute quantities of the expected acids, but the higher, less volatile aldehydes have never been found to react under ordinary conditions. Semmler,[7] however,

[1] Conant and Bartlett, *J. Amer. Chem. Soc.*, 1932, **54**, 2881; Westheimer, *ibid.*, 1934, **56**, 1962.
[2] Kharasch and Cooper, *J. Org. Chem.*, 1945, **10**, 46.
[3] Dewar, " The Electronic Theory of Organic Chemistry," Oxford, 1949, p. 116.
[4] Carter, *Organic Reactions*, 1946, Vol. III, p. 208.
[5] Fittig and Schneegans, *Annalen*, 1885, **227**, 79.
[6] Kietreiber, *Monatsh.*, 1898, **19**, 735.
[7] Semmler, *Ber.*, 1909, **42**, 584, 1161, 2014.

has shown that many aliphatic aldehydes give diacetates and enol acetates in high yield when heated with acetic anhydride with or without sodium acetate. This side-reaction might account for the failure of the expected main reaction.

TABLE 1. *Products obtained in the Perkin reaction.*

	Enol acetate (%)	Diacetate (%)	Residue	Acid (%)
Butanal	41	19	Some	0
2 : 2-Dimethylpropanal	0	0	0	0
3-Methylbutanal	(50)	(not given)	—	—
2-Ethylbutanal	55	25	—	0
Formyl*cyclo*hexane	46	10	Large	0
Heptanal	48 (50)	25 (25)	—	0
Octanal	42 (not given)	23 (not given)	—	0
Acraldehyde	0	32	Large	0
Crotonaldehyde	22	12 *	Large	0
Citral	35	12	Large	0
Cinnamaldehyde	0	0	—	42
Benzaldehyde	0	6	—	50

* Not entirely diacetate.

The Normal Perkin Reaction.—In the present work a number of aldehydes were heated with acetic anhydride or sodium acetate or with both. Heptanal, with acetic anhydride, gave the diacetate (21%) and the enol acetate (20%). Propanal, heated with sodium acetate for a very short time, gave the aldol (50%). The products obtained from various aldehydes with acetic anhydride and sodium acetate together, *i.e.*, under normal Perkin reaction conditions, were as listed in Table 1. Entries in parentheses refer to Semmler's work.[7]

It appears from this Table that saturated aliphatic aldehydes give largely diacetate and enol acetate, with some undefined high-boiling products but no acid. The only exception is the tertiary 2 : 2-dimethylpropanal which cannot form acetates but still gives no acid. Among the unsaturated aldehydes, crotonaldehyde and citral behave similarly. Their enol acetates must be derivatives of butadiene—in the case of crotonaldehyde, 1-acetoxy-1 : 3-butadiene (I). The diacetate fraction contained much dihydro-*o*-tolualdehyde (III) (isolated as its semicarbazone), previously obtained in the reaction of crotonaldehyde with amines.[8] Presumably the acetate (I) reacts in Diels–Alder fashion with the starting aldehyde to give an adduct (II) which loses acetic acid to give the product isolated. Acraldehyde cannot readily give an enol acetate: it did form a diacetate. The formation, together with cinnamic acid, of benzylidene diacetate from benzaldehyde under these conditions does not mean that it is an intermediate,[18] for this diacetate remained unchanged under the conditions of the Perkin reaction. Cinnamaldehyde gives only an acid. From the above it appears that only aromatic aldehydes, and related ones such as cinnamaldehyde, undergo the Perkin reaction. Aliphatic aldehydes either do not react or give acetates and various amounts of high-boiling material of unknown nature.
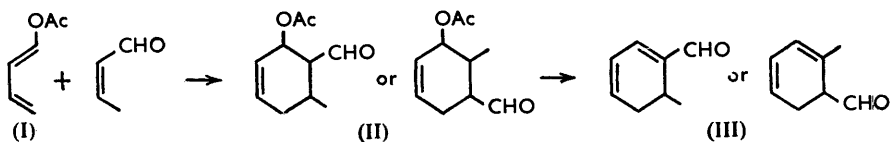
The Perkin–Oglialoro Reaction.—In this modification [9] of the Perkin reaction the acid component is phenylacetic anhydride or, more probably, the mixed anhydride of phenylacetic and acetic acid. Reaction with aryl aldehydes takes place very readily because of the activating effect of the phenyl group in stabilising by resonance the reacting

[8] Grundmann, *Chem. Ber.*, 1948, **81**, 513.
[9] Oglialoro, *Gazzetta*, 1878, **8**, 429; 1879, **9**, 428; 1880, **10**, 481.

anion, Ph·C̄H·CO$_2$Ac.   Table 2 shows that no acid was formed from aliphatic saturated aldehydes, but instead considerable amounts of enol acetate and high-boiling substances which were probably diacetate, diphenylacetate, and enol phenylacetate.

TABLE 2.   *Products (%) from aliphatic aldehydes in the Perkin–Oglialoro reaction.*

	Enol acetate	Acid		Enol acetate	Acid
Butanal	31	0	Crotonaldehyde	26	5
2 : 2-Dimethylpropanal	0	0	Citral	30	7
Formyl*cyclo*hexane	24	0	Cinnamaldehyde	0	61
Heptanal	26	Trace			

There is a claim [10] to have obtained α-phenylcrotonic acid from paraldehyde.   Unsaturated aldehydes gave small yields of acid; cinnamaldehyde gave a high yield of acid. The activation of the acid component, therefore, had enabled the Perkin reaction to take place more readily with aryl and to a slight extent with unsaturated aldehydes, but was not sufficient to bring about reaction with aliphatic aldehydes.

p-*Nitrophenylacetic Anhydride.*—The only successful use of saturated aliphatic aldehydes in the Perkin reaction giving good yields was that recorded by Häffcke and Becker [11] with sodium *p*-nitrophenylacetate and acetic anhydride at 60°.   Acetaldehyde gives a good yield of acid, propanal less, 2-methylpropanal much less, and 2 : 2-dimethylpropanal none at all.   This was attributed to increasing steric hindrance with the progressive introduction of methyl groups.

In the present work lower temperatures, 35—55°, were generally used.   The results are presented in Table 3.   Butanal condensed satisfactorily, but higher aldehydes hardly at all.   Unsaturated aldehydes reacted well.   Even the ketones, pyruvic acid and its ethyl ester, did so too.   Other ketones were unreactive, indicating that the lack of reactivity of ketones may well be due to steric hindrance, which is less in pyruvic acid.   The carboxyl group is less bulky than an alkyl group and in addition is highly electron-attractive and therefore activating towards the carbonyl group.   The product from pyruvic acid appears to be *p*-nitrophenylcitraconic anhydride (IV).   Ethyl pyruvate also reacts, but the product is a non-acidic substance C$_{12}$H$_{15}$O$_5$N and hence probably ethyl α-4-nitrobenzyl-lactate (V).
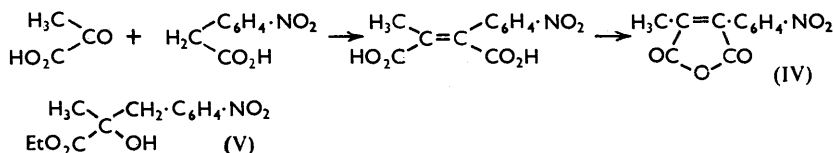
It is clear from the results listed in Table 3 that the further activation by the *p*-nitro-group has improved the reactivity of unsaturated aldehydes and has enabled the lower saturated ones to react.   The success of this reagent is undoubtedly due, not only to this activation, but also to the very low temperatures which can be used and which do not lead to diacetate and enol acetate.   It proves conclusively that aliphatic aldehydes will undergo the Perkin reaction, if somewhat reluctantly.   A study of comparative aldehyde reactivity based on this reaction is reported below.   It was mentioned above that benzylidene diacetate was unreactive in the Perkin reaction.   The same was found also to apply to acraldehyde diacetate, butanal enol acetate, and crotonaldehyde enol acetate in this reaction.   It can therefore be concluded that when acetate formation occurs the Perkin reaction is less likely to succeed.

Higher Aldehydes.—Table 3 shows the non-reactivity of higher aldehydes.   In other homologous series loss of reactivity and sudden variation in physical properties have occasionally been observed with increase in chain length, usually in the region of C$_5$ and C$_6$,

[10] Rupe, *Annalen*, 1909, **369**, 332.
[11] Häffcke and Becker, *J. Org. Chem.*, 1951, **16**, 863.

TABLE 3. *Products from aliphatic aldehydes and* p-*nitrophenylacetic anhydride.*

	This work	Acid (%) and Lit.		This work	Acid (%) and Lit.
Ethanal	—	55 [11]	Ethyl pyruvate	24 (ester)	—
Propanal	—	49 [11]	Acraldehyde	—	38 [a]
Butanal	35	—	Acraldehyde diacetate	0	—
Butanal enol acetate	0	—	Crotonaldehyde	56	40 [b]
2-Methylpropanal	—	12 [11]	Crotonaldehyde enol acetate	0	—
2 : 2-Dimethylpropanal	0	0 [11]	Citral	20	—
Pentanal	1	—	Acetone	0	—
Heptanal	Trace	—	*cyclo*Hexanone	0	—
Pyruvic acid	18	—			

[a] Thielcke and Becker, *J. Org. Chem.*, 1950, **15**, 1241. [b] Gunst, Tobkes, and Becker, *J. Amer. Chem. Soc.*, 1954, **76**, 3595.

e.g., the effect of chain length on the strength of fatty acids.[12] Newman[13] has commented on these variations and has used the term " rule of six " to describe them without attempting a full explanation. The non-reactivity of higher aliphatic aldehydes seems to be a further example of this puzzling rule.
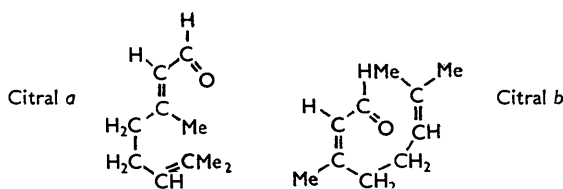
Citral *a*   Citral *b*

In order to test its applicability the aldehyde, citral, was used. It is known to consist of two isomers, citral *a* (*trans*) and citral *b* (*cis*). In citral *b* the tail of the molecule can coil back against the carbonyl group, whereas in citral *a* it cannot do so unless rotation of the formyl group out of conjugation with the αβ-double bond occurs, which is unlikely because of the loss of resonance energy involved. Citral obtained from lemon-grass oil was treated with acetic anhydride and sodium *p*-nitrophenylacetate, giving the expected acid which was separated, and the remaining citral was recovered. This was subjected once more to the same reaction, but only a trace of acid resulted. On a third treatment no acid was formed. The recovered citral had the expected b. p. and approximate analysis for citral *b*. It gave a semicarbazone of m. p. 170°. The starting citral, which was largely citral *a*, gave a semicarbazone of m. p. 164° (after many crystallisations). These values correspond to those in the literature.[14] It is thus clear that only citral *a* undergoes this Perkin reaction, although it is probably also somewhat hindered. Citral *b* does not react at all because it is more hindered owing to coiling of the chain against the carbonyl group.

Clearly the longer chains of higher aldehydes interfere sterically with the reactivity of the carbonyl group, but no convincing reason has so far been advanced as to how the tail is held in this conformation. Further striking examples of non-reactivity of aldehydes in the Perkin reaction due to increasing chain length will be given (*J.*, 1959, 732).

It is concluded that aliphatic aldehydes fail to undergo the Perkin reaction because of low reactivity and side-reactions. In the higher homologues, from pentanal, there is an additional hindering effect due to chain length.

Attempts to measure comparative carbonyl reactivity have given very contradictory results. For example, Michael[15] claims that aromatic form semicarbazones more readily than do aliphatic aldehydes, but Conant and Bartlett[1] and Westheimer[1] hold the reverse

[12] Bennet and Mosses, *J.*, 1930, 2364; Dippy, *J.*, 1938, 1222.
[13] Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 4783.
[14] Tiemann and Kerschbaum, *Ber.*, 1900, **33**, 877.
[15] Michael, *J. Amer. Chem. Soc.*, 1919, **41**, 393.

to be true. Stewart [16] found that acetaldehyde gives a bisulphite compound much more quickly than acetone, but Kharasch and Cooper [2] noted that phenylmagnesium bromide reacts much more readily with acetone than with acetaldehyde. The explanation probably is that some of these reactions occur in one stage and others in a sequence of stages. The latter applies to the Perkin reaction.

TABLE 4. *Comparative reactivities of aldehydes in reaction with acetic anhydride and sodium* p-*nitrophenylacetate at* 35°.

Aldehyde	Aromatic	Unsat.	Aldehyde	Aromatic	Unsat.	Aliphatic
o-Nitrobenzaldehyde	13,000	—	Crotonaldehyde	—	130	—
m-Nitrobenzaldehyde	6000	—	p-Anisaldehyde	*100*	—	—
p-Nitrobenzaldehyde	6000	—	p-*iso*Propylbenzaldehyde ...	100	—	—
o-Chlorobenzaldehyde	3300	—	p-Tolualdehyde	95	—	—
Furfuraldehyde	950	—	p-Ethylbenzaldehyde	80	—	—
p-Chlorobenzaldehyde	870	—	Ethanal....................	—	—	69
α-Naphthaldehyde	850	—	α-Methylacraldehyde	—	68	—
Cinnamaldehyde	—	730	Propanal	—	—	27
Benzaldehyde	390	—	Butanal	—	—	15
Acraldehyde	—	280	Heptanal	—	—	0
α-Methylcinnamaldehyde ...	—	140				

Rates for the ordinary Perkin reaction do not appear to have been measured, presumably on account of the high temperatures necessary and the heterogeneous conditions. Measurements have been made with pyridine as a solvent and catalyst,[17] but this is a different type of reaction. As the Perkin–Oglialoro reaction with sodium p-nitrophenylacetate takes place at room temperature with both aliphatic and aromatic aldehydes it is well suited for comparisons of reaction rates. Although the reaction mixture is heterogeneous and does not allow of absolute rate measurement, a competitive method in which two aldehydes in considerable excess compete for a limited amount of p-nitrophenylacetic anhydride at 35° was found to give sufficiently reproducible results.

When the two aldehydes compete, two acids are formed. These are easily freed from unchanged p-nitrophenylacetic acid. Since no side reactions take place at the low temperature used, the composition of the mixture can be determined by titration. Anisaldehyde, which is of intermediate reactivity, was given arbitrarily the value of 100. On this basis comparative reactivities are set out in Table 4. High accuracy is not claimed, but it is not necessary as the reactivities vary over a range of 1000 to 1. It is sufficient to place the aldehydes in order of reactivity.

Among aromatic aldehydes variation in the *para*-substituent has a marked effect, the order being $NO_2 > Cl > H > OMe >$ Alkyl, which is also the order of ability to remove electrons from the carbonyl group. The latter in turn becomes activated for addition. Hence addition to the carbonyl group seems to be the rate-controlling factor.

If this applies in all cases, aliphatic should be more reactive than aromatic aldehydes because in the latter the positive charge on the carbonyl group is spread by the mesomeric effect over the ring system,[3] but from the Table the contrary is manifestly the case. The only other possible rate-determining stage is elimination of water from the intermediate (VI). This would be aided by increasing the negative charge on $C_{(1)}$ and the positive charge on $C_{(2)}$. The nitro-group maintains a positive charge on $C_{(2)}$ in all com-

$$R \cdot C_6H_4 \cdot C_{(1)}H(OH) \cdot C_{(2)}H(CO_2H) \cdot C_6H_4 \cdot NO_2 \quad \text{(VI)}$$
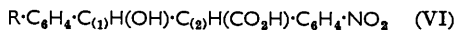
pounds in the series. The negative charge on $C_{(1)}$ would vary with ring substituents R in the order Alkyl $> H > NO_2$, which is the reverse of what is found. Hence elimination is not rate-controlling in aromatic aldehydes, but the slower stage, addition to the carbonyl group, is.

[16] Stewart, *J.*, 1905, **87**, 185.
[17] Buckles and Bremer, *J. Amer. Chem. Soc.*, 1953, **75**, 1487.

Aliphatic aldehydes react very slowly. This is not because the addition stage is slower. Indeed, it ought to be faster. It is because the elimination has become much slower. Elimination is assisted by conjugation in the product or transition state. Such conjugation is present in the cinnamic acids formed from aromatic aldehydes, extending from the ring through the double bond to the carbonyl group. It is present to a smaller extent in the conjugated acrylic acids formed from unsaturated aldehydes and is least in the simple acrylic acids from aliphatic aldehydes: the Table shows the intermediate position of unsaturated aldehydes. It also confirms that the low reactivity of aliphatic aldehydes is due to slow elimination of water.

The inertness of the higher aldehydes, due to coiling, is now confirmed by the low reactivity of butanal and the non-reactivity of heptanal.

Our method provides means of studying electronic and other effects in aromatic aldehydes. The nitro-group and chlorine atom are more effective the *ortho*-position, showing the predominance in both cases of inductive over mesomeric electron-displacement. The high reactivities of cinnamaldehyde and furfuraldehyde are due to decreased steric hindrance in the region of the carbonyl group, for such hindrance is known to affect the Perkin reaction [11] and accounts for the non-reactivity of tertiary aldehydes and most ketones: this is to some extent borne out by the comparatively low reactivity of α-methylcinnamaldehyde.

EXPERIMENTAL

1 : 1-*Diacetoxyheptane and* 1-*Acetoxyhept*-1-*en*-1-*ol.*—Heptanal (20 g.) was refluxed with acetic anhydride (60 ml.) for 8 hr. The product was treated with water and extracted with ether, and this in turn extracted with sodium carbonate solution. No acid was obtained. Distillation of the ether extract gave unchanged aldehyde (4·6 g.), enol acetate (5·1 g.), b. p. 80—90°/10 mm., and diacetate (8·1 g.), b. p. 110—115°/10 mm.

3-*Hydroxy*-2-*methylpentanal.*—Propanal (40 g.) and sodium acetate (11 g.) were heated together on a water-bath for 10 min., poured into water, and extracted with ether and the extract distilled. The fraction of b. p. 85—95°/10 mm. (19·7 g.) was the aldol (semicarbazone, m. p. 198°). Its 2 : 4-dinitrophenylhydrazone, m. p. 154°, did not depress the m. p. of propanal 2 : 4-dinitrophenylhydrazone.

1 : 1-*Diacetoxybutane and* 1-*Acetoxybut*-1-*en*-1-*ol.*—A mixture of butanal (58 g., 1 mol.), sodium acetate (0·5 mol.), and acetic anhydride (1·5 mol.) was refluxed for 8 hr., then poured into water, kept for some time, and extracted with ether. This extract was extracted with sodium carbonate solution, dried, and distilled. The fraction of b. p. 60—75° (10·6 g.) was unchanged aldehyde, that of b. p. 118—120° (37·6 g.) the enol acetate, and that of b. p. 80—82°/6 mm. 1 : 1-*diacetoxybutane* (Found: C, 55·5; H, 8·3. $C_8H_{14}O_4$ requires C, 55·2; H, 8·1%).

The other aldehydes listed in Table 1 were treated in the same fashion. The diacetate from benzaldehyde had m. p. 44·5°; it crystallised after removal of traces of benzaldehyde by means of sodium hydrogen sulphite. Most of the diacetates and enol acetates have already been described. The intermediate " diacetate " fraction from crotonaldehyde consisted largely of dihydro-*o*-toluataldehyde and gave its semicarbazone, m. p. 198° (Found: C, 60·5; H, 7·4; N, 23·2. Calc. for $C_9H_{13}ON_3$: C, 60·3; H, 7·3; N, 23·4%).

Perkin–Oglialoro Reactions (*Table* 2).—The aldehyde (1 mol.), freshly fused sodium phenylacetate (1 mol.), and acetic anhydride (2 mol.) were refluxed together for 5 hr. and poured on ice. The oil was extracted with sodium carbonate solution, to isolate any acid produced. The ethereal extract of the residue was washed, dried, and distilled. The first fraction after removal of ether was unchanged aldehyde, the next enol acetate. Higher fractions were not examined.

From crotonaldehyde there was obtained a small quantity of α-*phenylsorbic acid*, almost colourless needles, m. p. 144° (Found: C, 76·9; H, 6·2. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

From citral a small amount of 5 : 9-*dimethyl*-2-*phenyldeca*-2 : 4 : 8(or 9)-*trienoic acid* resulted, having m. p. 116° (from ethanol) (Found: C, 78·8; H, 8·1. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%).

Perkin Reactions using p-*Nitrophenylacetate* (*Table* 3).—The aldehyde (1 mol.), anhydrous sodium *p*-nitrophenylacetate (1 mol.), and acetic anhydride (3 mol.) were heated for 60 hr. at 35° (in some cases 55°) with stirring. A small amount of water was added and stirring continued for 2 hr. The whole was treated with concentrated hydrochloric acid and poured

into water. The ether extract was treated with sodium carbonate solution which on acidification gave the acid product. Any *p*-nitrophenylacetic acid present was removed by boiling water. The acid was recrystallised from aqueous ethanol.

The following acids were analysed: From butanal, 2-p-*nitrophenylhex-2-enoic acid*, m. p. 144°, very pale yellow plates (Found: C, 61·1; H, 5·6; N, 6·2. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·6; N, 6·0%). From crotonaldehyde, α-*p-nitrophenylsorbic acid*, m. p. 229°, pale yellow needles (Found: C, 61·6; H, 5·1. Calc. for $C_{12}H_{11}O_4N$: C, 61·8; H, 4·8%). This acid has been described by Gunst *et al.* (see Table 3). From pyruvic acid, used in the form of its sodium salt, p-*nitrophenylcitraconic anhydride*, yellow prisms, m. p. 124° (Found: C, 57·1; H, 2·7; N, 6·1. $C_{11}H_7O_5N$ requires C, 56·7; H, 3·0; N, 6·0%).

From ethyl pyruvate no acid resulted, but the neutral products afforded *ethyl α-4-nitrobenzyl-lactate* (24%), plates, m. p. 63° (Found: C, 56·8; H, 6·2. $C_{12}H_{15}O_5N$ requires C, 56·9; H, 6·0%).

Citral, b. p. 97°/2 mm., was obtained by vacuum-fractionation of lemon-grass oil. Its semicarbazone melted indefinitely about 130° but after 9 crystallisations at 164°, the value [14] for citral *a*. Citral (20 g.) was treated with sodium *p*-nitrophenylacetate and acetic anhydride in the standard manner but for 80 hr., giving 5 : 9-*dimethyl-2-p-nitrophenyldeca-2* : 4 : 8(or 9)-*trienoic acid*, yellow, m. p. 138° (Found: C, 67·9; H, 6·5; N, 4·0. $C_{18}H_{21}O_4N$ requires C, 68·5; H, 6·7; N, 4·4%). The neutral residue was then washed, dried, and distilled. A fraction (10·4 g.), b. p. 93—98°/2 mm., was citral. This was immediately subjected to reaction again. Acid (1·5%) resulted and a fraction (6 g.), b. p. 98—100°/4 mm., of citral *b* (Found: C, 77·8; H, 10·6. Calc. for $C_{10}H_{16}O$: C, 78·9; H, 10·6%), which gave a semicarbazone of m. p. 158° rising after two recrystallisations to 170°. On further subjection to the reaction this gave no acid.

Competitive Condensations.—Sodium *p*-nitrophenylacetate (1 mol.), acetic anhydride (5 mol.), and the two competing aldehydes (5 mol. each) were stirred together for 60 hr. at 35°. A stream of dry nitrogen was passed to prevent oxidation. The mixture was then treated with water and either (*a*) the mixture was steam-distilled to remove unused aldehydes and the solid extracted with alkali, or (*b*) the mixture was acidified with mineral acid and extracted with ether and the ether extract shaken with alkali. In all cases the alkaline extract was acidified. The precipitated mixture of acids was washed with boiling water to remove traces of *p*-nitrophenyl-acetic acid, then redissolved, reprecipitated, filtered off, washed, and dried at 80° for 24 hr. The equivalent weight was then determined by titration with 0·1N-sodium hydroxide. The aldehydes being compared were chosen so that the difference in their molecular weights was as great as possible.

To obtain the results given in the Table the following aldehydes were allowed to compete. Anisaldehyde against acraldehyde (2·81), crotonaldehyde (1·33), acetaldehyde (0·69), propanal (0·265), butanal (0·150), furfuraldehyde (9·46), 2-methylacraldehyde (0·68), and benzaldehyde (3·88); benzaldehyde against cinnamaldehyde (1·87), *p*-tolualdehyde (0·245), *p*-ethylbenz-aldehyde (0·197), *p-iso*propylbenzaldehyde (0·264), *o*-nitrobenzaldehyde (33·6), *m*- and *p*-nitro-benzaldehyde (15·57), *o*-chlorobenzaldehyde (8·42), *p*-chlorobenzaldehyde (2·24), α-naphth-aldehyde (2·20), and α-methylcinnamaldehyde (0·371). The figures in parentheses represent the ratio of the reactivity of the aldehyde relative to that of anisaldehyde or benzaldehyde. The values for acraldehyde and methylacraldehyde are low because of formation of polymer. Where the ratio is very large or very small excess of the less reactive aldehyde was used.

β-2′-*Furyl-α-p-nitrophenylacrylic Acid.*—From the reactions involving furfuraldehyde this *acid* was isolated as yellow needles, m. p. 241° (decomp.) (Found: C, 60·5; H, 3·5; N, 5·2. $C_{13}H_9O_5N$ requires C, 60·2; H, 3·5; N, 5·4%).

α-p-*Nitrophenyl-4-isopropylcinnamic Acid.*—This *acid* was isolated from the reactions involving *p-iso*propylbenzaldehyde, as pale yellow prisms (from aqueous alcohol), m. p. 233° (Found: C, 69·2; H, 5·5; N, 4·6. $C_{18}H_{17}O_4N$ requires C, 69·4; H, 5·5; N, 4·5%).

4-*Methyl-2-p-nitrophenyl-2* : 4-*pentadienoic Acid.*—This acid was obtained from reactions involving methylacraldehyde as light brown crystals (from aqueous ethanol), m. p. 164° [cf. Gunst *et al.* (see Table 3)] (Found: C, 61·8; H, 4·9. Calc. for $C_{12}H_{11}O_4N$: C, 61·8; H, 4·8%).

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