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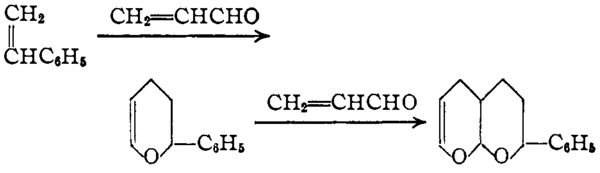
Reactions of Acrolein and Related Compounds. III. Addition of Olefins with a Discussion of Mechanism

BY CURTIS W. SMITH, DOUGLAS G. NORTON AND SEAVER A. BALLARD

Olefins such as isobutylene, diisobutylene, 1-hexene, styrene and α-methylstyrene have been added to conjugated carbonylic compounds such as acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone. Most of the adducts have been established as dihydropyrans derived from addition of the β-carbon of the aldehyde to the unsubstituted carbon of the olefin. The structures of the adducts described in this and the preceding two papers are not consistently in accord with those to be expected from a polar mechanism similar to that postulated for the Diels–Alder reaction. On the other hand a "divalent radical" mechanism, although not established, offers a better explanation for the orientation of reactants, if it is assumed that the stability of the intermediate diradical determines the direction of addition. From the literature known exceptions to the polar mechanism for the Diels–Alder reaction have been cited. It has been shown that a diradical mechanism similar to the above can be used to explain the direction of addition of dissimilar addenda.

Introduction

The addition of vinyl ethers and of unsaturated esters and methacrylonitrile to conjugately unsaturated carbonylic compounds has been presented in our two preceding papers.[1] In the present paper the addition of olefins is presented; the structures of many of the adducts are established as substituted dihydropyrans; and a generalized discussion of the reaction and its mechanism is given. The conditions for the addition of olefins were in general the same as those used previously; namely, the combined reactants were heated at 180–200° under autogenous pressure for one to two hours. Olefins such as isobutylene, diisobutylene, 1-hexene, styrene and α-methylstyrene have been added to conjugately unsaturated carbonylic compounds such as acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone. The conversion to products in this reaction were of the order of 10–25%. In addition to the primary adduct, I, from the addition of styrene to acrolein, a by-product, II, corresponding to the addition of two molecules of acrolein to one of styrene was obtained.



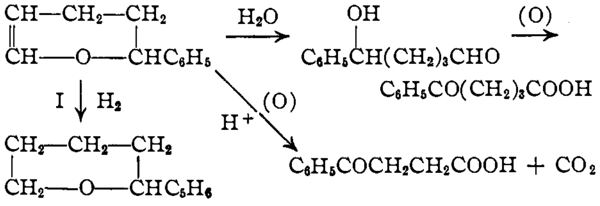
I II

Proof of Structure

In order to determine the direction of addition, the identity of a number of adducts has been established.

2-Phenyl-3,4-dihydro-2H-pyran.—The structure of the adduct of styrene and acrolein was established as 2-phenyl-3,4-dihydro-2H-pyran (I) by hydrolysis to δ-phenyl-δ-hydroxyvaleraldehyde followed by oxidation to γ-benzoylbutyric acid. This acid caused no depression in melting point when mixed with an authentic sample of γ-benzoylbutyric acid prepared from benzene and glutaric anhydride.

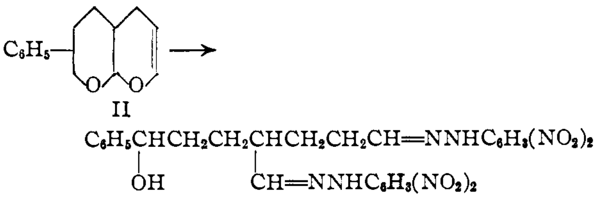
The phenyldihydropyran (I) absorbed hydrogen readily over Raney nickel to give a tetrahydropyran (III) the properties of which agreed with values cited by R. Paul[2] for 2-phenyltetrahydropyran prepared by the reaction of phenylmagnesium bromide with 2-bromotetrahydropyran.



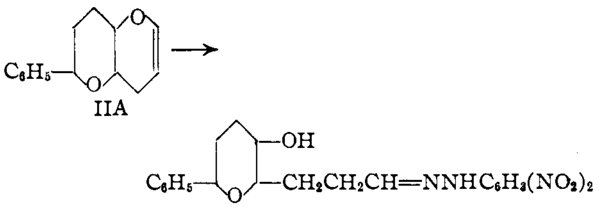
III

Acidic permanganate oxidation of the adduct gave β-benzoylpropionic acid and carbon dioxide. This behavior is consistent with that to be expected from Formula I.

At least a major portion of the adduct of two molecules of acrolein and one of styrene is indicated to be 2-phenyl-2,3,4,4a,5,8a-hexahydro-1,8-dioxanaphthalene (II). This adduct gave a mono- and a bis-2,4-dinitrophenylhydrazone. The infrared absorption spectrum of the monohydrazone indicated the presence of an aldehyde group.



The isomeric IIA would be expected to give only a monohydrazone which would not have an aldehyde linkage.



2-*n*-Butyl-3,4-dihydro-2H-pyran.—The following outline shows the proof of structure of the adduct of 1-hexene and acrolein.

Hydrogenation of the adduct gave a derivative whose boiling point, refractive index and infrared absorption were in agreement with 2-*n*-butyltetra-

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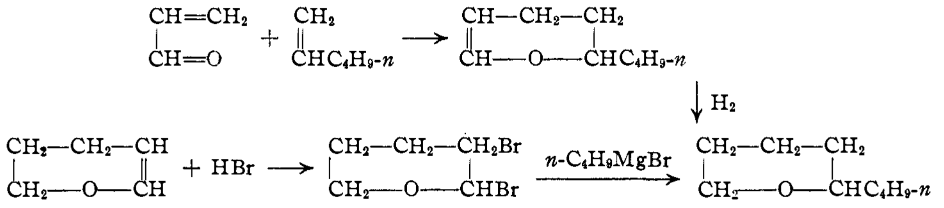
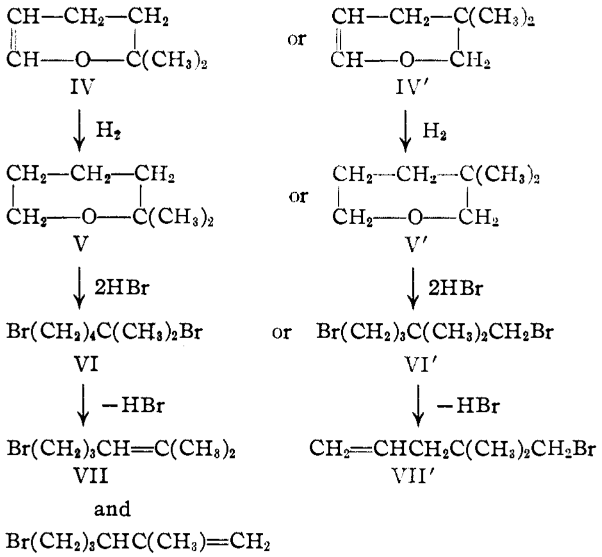
[1] C. W. Smith, D. G. Norton and S. A. Ballard, THIS JOURNAL, **73**, 5267 (1951).

[2] R. Paul (a) *Compt. rend.*, **206**, 1028 (1938); (b) **198**, 1246 (1934); (c) *Bull. soc. chim.*, [5] **2**, 311 (1935).



hydropyran prepared from dihydropyran by addition of hydrogen bromide and subsequent reaction with *n*-butylmagnesium bromide according to the method of Paul.[2a]

2,2-Dimethyl-3,4-dihydro-2H-pyran.—The adduct of isobutylene and acrolein was shown by a series of degradation reactions to be 2,2-dimethyl-3,4-dihydro-2H-pyran (IV) and not 3,3-dimethyl-3,-4-dihydro-2H-pyran (IV′).



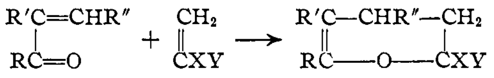
The dihydropyran (IV) was hydrogenated catalytically to give the dimethyltetrahydropyran (V). Treatment of the tetrahydropyran with dry hydrogen bromide in a sealed tube for two hours at 70° gave a dibromide (VI). The dibromide (VI) lost hydrogen bromide on heating with a catalytic amount of hydrobromic acid. The infrared absorption[3] of the olefinic bromide (VII) indicated that the product was a mixture of compounds with double bonds of the types $R_2C{=}CH_2$ and $RCH{=}CR_2$ to be expected from tertiary halides.

When the dibromide (VI) was allowed to stand in 0.5 *N* alcoholic sodium hydroxide for 30 minutes, it was found that approximately half the bromine had become ionic. From these results there seems little doubt that the dibromide is 2,6-dibromo-2-methylhexane (VI) which contains a primary and a labile tertiary bromide rather than 1,5-dibromo-2,2-dimethylpentane (VI′) which contains a primary and a neopentyl bromide. From this evidence it appears that the starting material in this series of reactions was 2,2-dimethyl-3,4-dihydro-2H-pyran (IV).

Hydrolysis of the Substituted Dihydropyrans.—Two adducts, 2-phenyl-3,4-dihydro-2H-pyran and 2,4-dimethyl-2-phenyl-3,4-dihydro-2H-pyran have been hydrolyzed with 10% sulfuric acid. Lowering the acid concentration decreased the rate of hydrolysis markedly. From these reactions δ-phenyl-δ-hydroxyvaleraldehyde and δ-phenyl-δ-methyl-δ-hydroxycaproaldehyde were obtained. By proper choice of addenda this reaction furnishes a path for the preparation of other substituted δ-hydroxyvaleraldehydes.

Generalizations on the Addition Reaction.—Preparatory to a discussion of reaction mechanism, the following generalizations have been drawn on the addition of ethylenic to conjugated carbonylic compounds reported in this and the preceding two papers[1] of this series.

Direction of Addition.—Concerning the direction of addition, it has been observed that in every case the oxygen of the conjugated carbonyl has become attached to the substituted carbon of the ethylenic compound.



Assuming a polar mechanism, it might be expected that the direction of addition would vary with different groups as X and Y especially in view of the variety of groups which have been used. Electropositive, $-CH_3$, $-C_4H_9$-*n*, and electronegative, -CN, $-COOCH_3$, $-OCH_3$, $-SC_6H_5$, $-C_6H_5$ groups have been used. Groups such as -CN, $-COOCH_3$, -CHO which cause meta orientation of cations into the benzene ring and groups such as $-OCH_3$, $-C_6H_5$, $-CH_3$ which cause para and ortho substitution have been used as X and Y. However, in all cases the observed direction of addition was the same.

Reaction Rate.—In a consideration of the factors determining the reaction rate, the ethylenic addenda will be considered first and then the carbonylic addenda. In order to furnish a basis for comparison, Table IV has been drawn up listing addenda to acrolein in decreasing yield. In these similar reactions it is felt that there is a positive correlation between yield and reaction rate. Reactions of acrolein with vinyl ethers and unsaturated esters and nitriles are taken from our previous work.[1] These figures represent essentially complete reaction, *i.e.*, only a very small percentage of acrolein was recovered.

From Table IV it can be seen that the vinyl ethers and phenyl vinyl sulfides, which contain electron-rich double bonds, gave the highest yields, and the acrylates and methacrylonitrile, with electron-poor ethylenic bonds, gave the lowest yields. As discussed in the section on mechanism this is the behavior to be expected due to the electron poor ethylenic bond of acrolein. The yields with olefins are somewhat lower than might be expected from a regular transition based on this principle of addition.

In regard to the relation between the nature of the carbonylic addenda and the conversion to

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[3] For general principles see R. S. Rasmussen, *Fortschr. Chem. org. Naturstoffe*, **5**, 348 (1948).

TABLE I

ADDITION OF OLEFINS TO α,β-UNSATURATED CARBONYLS

Addendum A[f]	Addendum B[f]	Temp., °C.	Time, hr.	Adduct	Conversion to adduct[i]	Yield[j]
Acrolein[a]	Isobutylene	220	2	I	11	12A,[d] 72B[e]
Acrolein[a]	1-Hexene	180–210	3	II[h]	6	....
Acrolein[a]	Diisobutylene	200	2.5	III	9	15A, 42B
Acrolein[a]	Styrene[b]	155	1.5	IV	15	24A
				V	15	24A
Acrolein[a]	α-Methylstyrene	180	1	VI	23	37B
				X[g]	10	10B
Methacrolein[a]	α-Methylstyrene	175	1	VII	12	52B
Crotonaldehyde	α-Methylstyrene	216	1.5	VIII	17	42B
Crotonaldehyde[c]	α-Methylstyrene	216	1.5	VIII	18	45B
Methyl vinyl ketone[a]	α-Methylstyrene	180	1	IX	5	5B

[a] The acrolein, methacrolein, and methyl vinyl ketone used in these experiments have been inhibited with 0.1% hydroquinone. [b] The styrene was inhibited with 1% hydroquinone. [c] In this experiment freshly distilled uninhibited reactants were used and 1% of benozyl peroxide was added. [d] The letter "A" means the yield figure is based on unsaturated carbonyl. [e] The letter "B" means the yield figure is based on olefin. [f] Equimolar quantities of the two reactants were used in every case. [g] This product, b.p. 140–170° (1 mm.), was not analyzed. By analogy to V the product may be 2-methyl-2-phenyl-2,3,4,4a,5,8a-hexahydro-1,8-dioxanaphthalene. [h] Analysis indicated this product 2-*n*-butyl-3,4-dihydro-2H-pyran to contain acrolein dimer which was subsequently removed by hydrogenation and distillation to leave 2-*n*-butyltetrahydropyran discussed in the experimental section. [i] Conversion to adduct = moles of adduct/moles of addendum charged. [j] Yield = moles of adduct/moles of addendum consumed.

TABLE II

PROPERTIES AND ANALYSES

	Adduct	Boiling point °C.	Mm.	n^{20}_D	d^{20}_4	Analyses, % Theory Carbon	Theory Hydrogen	Found Carbon		Found Hydrogen	
I	2,2-Dimethyl-3,4-dihydro-2H-pyran	52–58	100	1.4371	....	74.95	10.79	74.75	74.65	10.78	10.74
III	2-Methyl-2-neopentyl-3,4-dihydro-2H-pyran	106–109	50	1.4549	....	78.51	11.98	78.35	78.29	11.90	11.92
IV	2-Phenyl-3,4-dihydro-2H-pyran	87	3.5	1.4519	....	82.46	7.57	82.32		7.57	
V	2-Phenyl-2,3,4,4a,5,8a-hexahydro-1,8-dioxanaphthalene	140–142	0.02	....	....	77.75	7.46	77.90	77.91	7.48	7.47
VI	2-Methyl-2-phenyl-3,4-dihydro-2H-pyran	70	1.5	1.5332	1.0280	82.72	8.10	82.59	82.59	8.12	8.12
VII	2,5-Dimethyl-2-phenyl-3,4-dihydro-2H-pyran	72–74	1	1.5280	1.0085	82.9	8.6	82.5	82.6	8.9	8.9
VIII	2,4-Dimethyl-2-phenyl-[a] 3,4-dihydro-2H-pyran	69–71 113–115	1 10	1.5252	1.0031	82.94	8.57	82.20	82.23	8.60	8.59
IX	2,6-Dimethyl-2-phenyl-[a] 3,4-dihydro-2H-pyran	103–106	1	1.5330	0.9980	82.94	8.57	82.16	82.15	8.55	8.53

[a] These samples stood for about two months before analysis. The low values found for carbon content may have been due to absorption of water or oxygen. In this work when the sample was allowed to stand for several weeks before analysis carbon values were consistently low by 0.2–0.4%. When analysis was carried out on the freshly distilled sample no difficulties were experienced.

TABLE III

DERIVATIVES

Adduct No.	2,4-Dinitrophenylhydrazone of	Melting point, °C.	Formula	Analyses, % Theory	Found	
I	δ-Hydroxy-δ-methylcaproaldehyde	100.6–101.6	$C_{13}H_{18}O_5N_4$	N, 18.1	N, 17.9	17.9
III	5-Hydroxy-5,7,7-trimethyloctanal	98–100	$C_{17}H_{26}O_5N_4$	N, 16.0	N, 16.1	16.1
IV	δ-Phenyl-δ-hydroxyvaleraldehyde	97–98	$C_{27}H_{18}O_5N_4$	C, 57.0 H, 5.1 N, 15.6	C, 57.1 H, 5.3 N, 15.7	
V	4-Formyl-7-hydroxy-7-phenylheptanal (mono-2,4DNP)[a]	85.4–85.7	$C_{20}H_{22}O_6N_4$	N, 13.52	N, 13.35	
	Bis-2,4-DNP	111.5–113.5	$C_{26}H_{26}O_9N_8$	N, 18.8	N, 18.1	18.2
VI	δ-Phenyl-δ-hydroxycaproaldehyde	91.5–93.5	$C_{18}H_{20}O_5N_4$	N, 15.1	N, 14.8	14.8

[a] Infrared absorption spectrum of this derivative showed the presence of an aldehyde linkage.

product it may be noted that dimerization of the conjugated carbonyl is competing with the desired reaction and the less reactive the carbon to carbon double bond of the compound being added or the more reactive the conjugated carbonylic compound the greater will be the amount of dimerization.

TABLE IV

Ethylenic addenda	Yield, %[a]
$CH_2{=}CHOCH_2CH(CH_3)_2$	85
$CH_2{=}CHOCH_3$	84
$CH_2{=}CHSC_6H_5$	77
$CH_2{=}CHOC_6H_5$	51[b]
$CH_2{=}CHCHO$	55
$CH_2{=}C(CH_3)CO_2CH_3$	40
$CH_2{=}C(CH_3)C_6H_5$	23
$CH_2{=}CHC_6H_5$	15
$CH_3{=}C(CH_3)_2$	11
$CH_2{=}C(CH_3)CH_2C(CH_3)_3$	9
$CH_2{=}CH(CH_2)_3CH_3$	6
$CH_2{=}C(CH_3)CN$	5
$CH_2{=}CHOCOCH_3$	5
$CH_2{=}CHCOOCH_3$	3

[a] Owing to the fact that many of these experiments are on a small scale these figures may be in error as much as ±5%. These figures take no credit for recovered acrolein or ethylenic addenda. [b] Owing to loss of material for which no credit was taken; the yield in this reaction is undoubtedly much higher than reported.

Table V brings out this point. (For this point the experimental conditions listed are of no consequence.)

TABLE V

ADDITIONS TO METHYL VINYL ETHER

Conjugated carbonylic addenda	Temp., °C.	Time, hr.	Conversion, % To product	To dimer
Crotonaldehyde	185	2	21	0
Crotonaldehyde	225	3	64	0
Acrolein	180	1	84	3
Methacrolein	190	2	21	55

From this table it can be seen that crotonaldehyde adds methyl vinyl ether less rapidly than does acrolein or methacrolein. However, due to the fact that crotonaldehyde shows little or no tendency to dimerize satisfactory conversions to product may be obtained in high yield by the use of higher temperature and longer reaction time.

Effect of Substitution.—Two observations indicate that substitution on the unsaturated terminal carbon atom of the ethylenic addendum hinders its addition to an unsaturated aldehyde: (1) crotonaldehyde exhibits much less tendency to dimerize than does acrolein; this is undoubtedly due at least in part to inactivity of the ethylenic bond caused by the presence of the β-methyl group. (2) A much lower yield was observed in the addition to alkoxydihydropyrans than in the addition of acrolein to vinyl alkyl ethers.

Substitution at the β-carbon of the unsaturated aldehyde interferes with the addition of ethylenic compounds. Thus, the addition of methyl vinyl ether to crotonaldehyde does not proceed as completely as the addition to acrolein (see Table V). Apparently, substitution of two methyl groups at the β-position as in mesityl oxide inhibits addition of vinyl ethers.

Reaction Mechanism

A detailed consideration of the characteristics of the addition of ethylenic to conjugated carbonylic compounds leads one to suspect that it proceeds by the same mechanism which accounts for the conventional Diels–Alder reaction. Of particular significance in this connection are the similar reaction conditions, the lack of catalysis, and the reversibility at high temperatures. Operating on the assumption that the reaction mechanisms are identical, and in view of the general lack of agreement as to the intimate mechanism of the Diels–Alder reaction, it is of particular importance to demonstrate how the evidence accumulated on the reactions of acrolein, as well as information which has appeared recently in the literature, tend to substantiate or negate proposed mechanisms for the Diels–Alder reaction.

In the following section it will be pointed out that in the direction of addition of several ethylenic addenda to acrolein and other conjugated carbonylic addenda there are numerous examples of exceptions to a polar mechanism. Furthermore, several examples of conventional Diels–Alder reactions, to be given later, are not in agreement with the polar mechanism.

The polar mechanism[4–8] assumes that the polarity of the reactive centers of both the diene and dienophile as determined by conventional ionic reactions, such as addition of hydrochloric acid, will determine the direction of addition. We realize that the direction of addition in the majority of the Diels–Alder reactions is in accord with a polar mechanism but with the considerable number of exceptions which now exist, we felt that some other mechanism must be sought.

Consequently, we have turned to consideration of a radical mechanism which has been previously suggested by others who did not attempt to correlate direction of addition of dissimilar addenda. It appears that the direction of addition of ethylenic to conjugated carbonylic compounds as well as the addition of dissimilar addenda in the Diels–Alder reaction are consistently in accord with a radical mechanism.

The following is a list of products from Diels–Alder type reactions whose structures are contrary to those which would have been predicted assuming a polar mechanism: the thermal dimers of acrolein,[9] methyl vinyl ketone,[10] methacrolein,[11] 1-vinylnaphthalene,[6] 1-cyano-1,3-butadiene[12] and 2-cyano-1,3-butadiene[13]; acrylic ester adduct of 1-cyanobutadiene[14]; acrylic acid and ethyl acrylate to 1-(*p*-bromophenyl)-1,3-butadiene and 1-(*p*-nitrophenyl)-1,3-butadiene[15]; adducts of citraconic anhydride to 1-vinylnaphthalene and to 1-vinyl-6-methoxynaphthalene[16]; ethyl sorbate and phenyl vinyl ketone.[17]

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(4) B. J. F. Hudson and R. Robinson, *J. Chem. Soc.*, 715 (1941).

(5) J. S. Meek and J. W. Ragsdale, THIS JOURNAL, **70**, 2502 (1948).

(6) G. B. Bachman and N. C. Deno, *ibid.*, **71**, 3062 (1949).

(7) R. B. Woodward, *ibid.*, **64**, 3058 (1942).

(8) (a) M. C. Kloetzel, "Diene Synthesis I," (b) H. L. Holmes, "Diene Synthesis II" in "Organic Reactions," by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1948, Vol. IV. pp. 8, 64.

(9) K. Alder, H. Offermanns and E. Reuden, *Ber.*, **74B**, 905 (1941).

(10) K. Alder and E. Reuden, *ibid.*, **74B**, 920 (1941).

(11) R. R. Whetstone, U. S. Patent 2,479,283 (1949).

(12) H. R. Snyder and G. I. Poos, THIS JOURNAL, **71**, 1395 (1949).

(13) C. S. Marvel and N. O. Brace, *ibid.*, **71**, **37** (1949).

(14) H. R. Snyder and G. I. Poos, *ibid.*, **72**, 4104 (1950).

(15) G. A. Ropp and E. C. Coyner, *ibid.*, **72**, 3960 (1950).

(16) W. E. Bachmann and L. B. Scott, *ibid.*, **70**, **1462** (1948).

(17) C. F. H. Allen, A. C. Bell, A. Bell, and J. Van Allan, *ibid.*, **62**, 656 (1940).

Alder, Schumacher and Wolff[18] established the structure of the adduct of 1,3-butadiene-1-carboxylic acid and acrylic acid as tetrahydro-*o*-phthalic acid and the adduct of 1,3-butadiene-1-carboxylic acid chloride and acrylyl chloride as tetrahydro-*o*-phthaloyl chloride. These authors recognized clearly that these additions were contrary to the polar mechanism and stated without elaboration that a "(Krypto)-radikalischen" mechanism might better represent the reaction.

Turning to a consideration of the radical mechanism, Coyner and Hillman[19] have postulated a "divalent radical" mechanism for the dimerization of acrylonitrile (clearly contrary to a polar mechanism) to give 1,2-dicyanocyclobutane. They also proposed that acrolein dimerized by a similar mechanism.

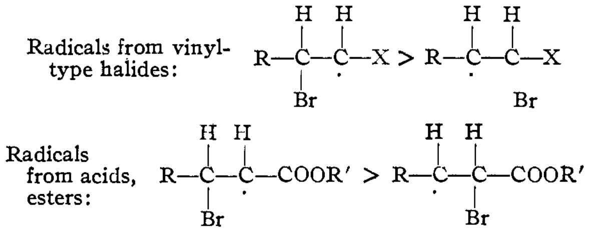
Kistiakowsky and his collaborators[20] have postulated a divalent radical mechanism for the Diels–Alder reaction in the gas phase. The evidence is based on a study of the frequency factor and activation energy of the gas-phase dimerization of butadiene. The observed frequency factor 1.8 × 10¹⁰ agreed closely with the calculated value of 0.9 × 10¹⁰. The activation energy (about 25 calories) was believed to be too low for an ionic mechanism and consistent only with a divalent radical mechanism.

Examination of the data both on reaction of acrolein and of true dienes with dieneophilic addenda, in light of known free radical reactions, has encouraged us to propose a system by which the direction of addition can be predicted. Although this system can easily form the basis for a true reaction mechanism we feel that insufficient independent evidence has been accumulated as yet to formalize the system as a mechanism.

As a first step in this scheme one or both of the addenda may be converted to a diradical under thermal activation. Once a diradical (1,4- or 1,2-) is formed it may then add to another unsaturated linkage, diene or ethylenic compound, to generate a new, larger, more-stable diradical. This direction of addition of radical to olefin is the controlling factor in determining the ultimate structure of the product since the only remaining step is ring closure of the resultant 1,6-diradical. The direction of addition of radicals to ethylenic compounds is well established and need not be discussed here. Obviously, the nature of the ethylenic compound exerts an orienting effect in the addition with the radical, but the exact nature of the factors affecting this orientation are not clear. One useful generalization for predicting the direction of addition, reported by Mayo and Walling,[21] is that the product radical of greatest stability will be formed. In the addition of bromine radicals, the following orders of decreasing stabilities of free radicals are required.

Radicals from hydrocarbons:

tertiary > secondary > primary



Radicals from vinyl-type halides:

$$\mathrm{R{-}\overset{H}{\underset{Br}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}X > R{-}\overset{H}{\underset{\cdot}{C}}{-}\overset{H}{\underset{Br}{C}}{-}X}$$

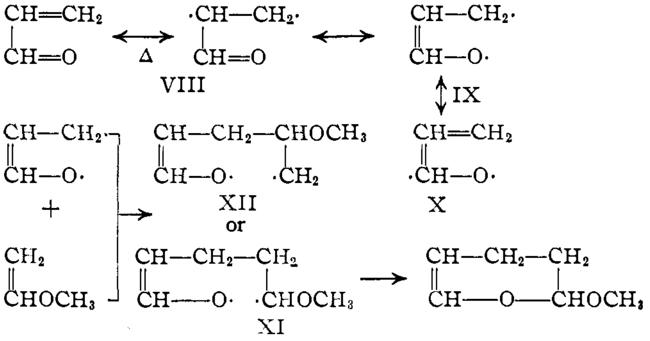
Radicals from acids, esters:

$$\mathrm{R{-}\overset{H}{\underset{Br}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}COOR' > R{-}\overset{H}{\underset{\cdot}{C}}{-}\overset{H}{\underset{Br}{C}}{-}COOR'}$$

Another and probably parallel generalization is that radicals add to the end of conjugated systems.

On this basis in the addition of an ethylenic compound with a diene or a conjugated carbonylic compound, the same adduct should be formed whether the 1,4- or 1,2-diradical initiates the addition. However, because of its greater ease of formation the 1,4-diradical would be expected to initiate the majority of the additions. Collision between two activated molecules seems unnecessary and improbable.

Applying these principles to the addition of ethylenic compounds to conjugated carbonylic compounds we have the following scheme with acrolein and methyl vinyl ether



Considering the activated diradical from acrolein three resonance hybrids (VIII, IX, X) are involved. The secondary radicals in hybrids VIII and X would be expected to be less reactive[18] than the primary radicals in IX. The literature contains little or no information on the comparative reactivity of the alkyl versus the alkoxy radical of IX. For this reaction scheme the alkyl radical would need to be the more reactive. The next step in this scheme is the addition of the activated β-carbon atom of acrolein to the vinyl ether to generate the 1,6-diradical XI or XII depending upon the direction of addition. Intermediate XI contains a secondary radical and is favored over XII which contains only primary radicals. This same reasoning can be applied to the addition of methyl acrylate to acrolein in which the carbomethoxy radical replaces the methoxyl radical. The product from addition of the vinyl ether is in accord with a polar mechanism while the product from the addition of methyl acrylate is not.

Turning to the reactions of 1-vinylnaphthalene we consider first a reaction in accord with the polar mechanism[4] and then one contrary.[16]

In 1-vinylnaphthalene (XIII) resonance possi-

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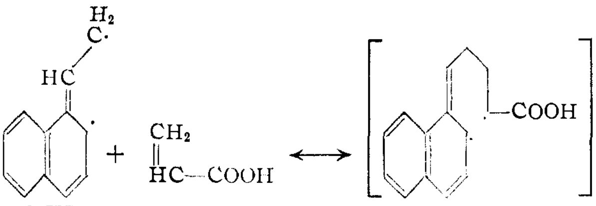
[18] K. Alder, M. Schumacher and O. Wolff, *Ann.*, **564**, 79 (1949).

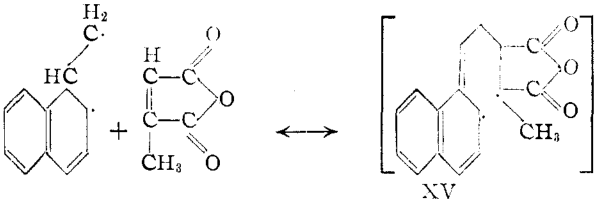
[19] E. C. Coyner and W. S. Hillman, This Journal, **71**, 324 (1949).

[20] J. B. Harkness, G. B. Kistiakowsky and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937); G. B. Kistiakowsky and W. W. Ransom, *ibid.*, **7**, 725 (1939); G. B. Kistiakowsky and J. R. Lacher, This Journal, **58**, 123 (1936).

[21] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).



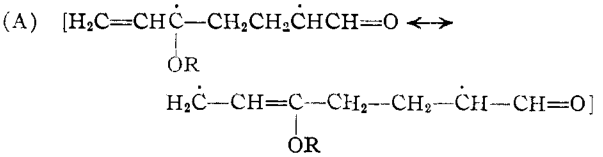
XIII XIV



XV

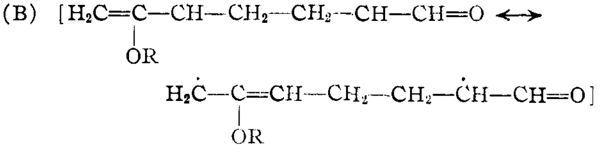
bilities of the single electron on the ring would dissipate its reactivity and thus the β-carbon should be the more reactive center. With XIV we have the intermediate formation of a secondary favored over that of a primary radical while with XV we have the favored intermediate tertiary rather than a secondary radical.

Other adducts of established structure are those of acrolein and of methyl 3,4-dihydro-1-naphthoate with 2-ethoxy- and 2-methoxybutadiene.[22] These reactions can be given similar treatment. Since in the reactions of radicals the direction of addition is determined by the product radical of greatest stability,[21] the same product is obtained whether the addition is initiated by the acrolein or the diene.

(A) 

$$[H_2C{=}CH\underset{\displaystyle OR}{\dot{C}}{-}CH_2CH_2\dot{C}HCH{=}O \longleftrightarrow H_2\dot{C}{-}CH{=}\underset{\displaystyle OR}{C}{-}CH_2{-}CH_2{-}\dot{C}H{-}CH{=}O]$$

XVI

(B) 

$$[H_2C{=}\underset{\displaystyle OR}{C}{-}\dot{C}H{-}CH_2{-}CH_2{-}\dot{C}H{-}CH{=}O \longleftrightarrow H_2\dot{C}{-}\underset{\displaystyle OR}{C}{=}CH{-}CH_2{-}CH_2{-}\dot{C}H{-}CH{=}O]$$

The upper pair (A) with resonance between a primary and tertiary radical is favored over the lower pair (B) with resonance between a primary and secondary radical. Ring closure of XVI gives the product of established structure. The same reasoning as above applies to the adduct of isoprene and 2,6-dimethoxy-4-*n*-amylcinnamic acid.[23]

The fact that radical considerations are thought to control the direction of addition is not taken to mean that polar effects are inoperative. Earlier in this paper it was shown that ethylenic compounds like vinyl ethers and phenyl vinyl sulfide which have strongly nucleophilic terminal carbon atoms give the highest yields on addition to acrolein the terminal carbon of which is strongly electrophilic. The lowest yields in additions to acrolein were obtained in the addition of acrylates or methacrylonitrile with electrophilic terminal carbon atoms. Although this appeared as a general trend with the addenda to acrolein there were certain irregularities. In the Diels–Alder reaction it has been observed that the reaction of dienes and ethylenic compounds is favored when these entities have different electron densities. This phenomenon may well be related to similar behavior in radical-catalyzed copolymerization.

From data in the literature there are at least two important factors determining the rate at which individual monomers enter into copolymerization. Alfrey and Price[24] have set up a system for evaluating these factors in a quantitative manner. One factor " 'general monomer reactivity'...is apparently related to possibilities for stabilization in a radical adduct." The other "takes account of polar factors influencing copolymerization." In general, other factors being equal, the greater the difference in polarity of the reactive centers of the two monomers the greater their tendency to copolymerize (radical reaction). These same two factors may well be operative in the Diels–Alder reaction especially in view of the fact that copolymerization is an important side reaction in many Diels–Alder reactions and sometimes is the predominant reaction. Harkness, Kistiakowsky and Mears[20] consider that the concomitant polymerization and dimerization of 1,3-butadiene may proceed by similar mechanisms if the radicals involved have a life long enough to undergo further addition. The fact that the tendency of a styrene to react with maleic anhydride is enhanced by an alkoxyl group para to the unsaturated side chain, but that a similar group in the meta position has no such effect has been considered[4] as support for the polar mechanism for the Diels–Alder reaction. This observation may be considered as additional evidence for the operation of polar effects in the Diels–Alder reaction. However, it is not inconsistent with the radical mechanism as presented herein which recognizes the important role polar effects may play.

According to the present scheme radical considerations control the direction of addition and electronic plus radical effects determine the reaction rate. It is conceivable that in certain cases one or the other of the electronic or radical effects may play the dominant role in controlling the reaction rate. From an examination of Table IV (styrene *versus* α-methylstyrene; methyl methacrylate *versus* methyl acrylate; and 1-hexene *versus* isobutylene) it appears that the presence of an additional methyl group on the substituted carbon atom of the ethylenic compound increases the rate of addition to acrolein. This behavior may be due to one or both of the following possibilities: (1) The intermediate 1,6-diradical in the cases with the additional methyl group contains the more stable tertiary rather than a secondary radical; (2) the presence of the additional methyl group increases the electron density of the ethylenic compound and by this means increases the reaction rate. It would be of interest to investigate further the only case we know of addition appar-

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[22] H. Fiesselmann, *Ber.*, **75**, 881 (1942).

[23] R. Adams and R. B. Carlin, THIS JOURNAL, **65**, 360 (1943).

[24] T. Alfrey and C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

ently contrary to the present reaction scheme, *i.e.*, the meta type addition of acrylyl chloride to β-chloroethyl sorbate and sorbyl chloride.[25,26]

Experimental

2-Phenyl-3,4-dihydro-2H-pyran (I).—The following experiment is offered as a detailed example for the experiments in Table I. A mixture of 104 g. (1 mole) of styrene, 56 g. (1 mole) of acrolein and 1 g. of hydroquinone was heated in a sealed glass tube at 155° for 1.5 hours. Distillation gave 24 g. of a material boiling at 87° (3.5 mm.), n^{20}_{D} 1.4519 and 16 g. of another substance boiling at 140–142° (0.02 mm.) along with 15 g. of acrolein, 31 g. of styrene and 71 g. of polymer. The infrared absorption spectrum of the low boiling material showed only one band at 6.05 μ in the double bond region (indicating the presence of a carbon to carbon double bond and the absence of an aldehyde linkage). As 2-phenyl-3,4-dihydro-2H-pyran, the lower boiling material represents a 15% conversion to product in a 24% yield based on acrolein. For analysis see Table II.

The material boiling at 140–142° (0.02 mm.) was indicated to be 2-phenyl-2,3,4,4a,5,8a-hexahydro-1,8-dioxanaphthalene by the formation of a bis-2,4-dinitrophenylhydrazone derivative (see Table III) and as such represents a 15% conversion to product and 24% yield based on acrolein. For analysis see Table II.

Hydrolysis of 2-Phenyl-3,4-dihydro-2H-pyran.—A mixture of 32 g. of 2-phenyl-3,4-dihydro-2H-pyran, 64 g. of 10% sulfuric acid and 110 ml. of dioxane was heated on the steam-cone with stirring for two hours. The mixture was cooled and extracted with petroleum ether. The extract was washed with sodium bicarbonate and dried. Distillation from a Claisen flask gave, as the only product, 17.5 g. (49% yield) of δ-phenyl-δ-hydroxyvaleraldehyde which was collected chiefly at a temperature of 106–108° (0.06 mm.). The product crystallized in the receiver. After recrystallization from benzene–petroleum ether the δ-phenyl-δ-hydroxyvaleraldehyde melted at 63.5–64°. The infrared absorption of this material indicated it to exist almost completely as the cyclic hemiacetal, 2-phenyl-6-hydroxytetrahydropyran.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.17; H, 7.94.

γ-Benzoylbutyric Acid.—Two grams of δ-phenyl-δ-hydroxyvaleraldehyde was suspended in 30 ml. of water containing two drops of 10% sodium hydroxide. A saturated solution of potassium permanganate was added portionwise with shaking at room temperature until the permanganate color persisted for 30 minutes. The mixture was acidified with dilute sulfuric acid and a 30% solution of sodium bisulfite was added until the manganese dioxide was all dissolved. The crystalline product was separated by filtration and recrystallized from benzene. Two grams (90% yield) of γ-benzoylbutyric acid, m.p. 126.5–127°, was obtained.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.87; H, 6.33.

A mixture of the above product with γ-benzoylbutyric acid prepared from benzene and glutaric anhydride[27] gave no depression in melting point.

Oxidation of 2-Phenyl-3,4-dihydro-2H-pyran.—When 1 ml. of 2-phenyl-3,4-dihydro-2H-pyran was added to a solution of 3 ml. of sulfuric acid in 30 ml. of water followed by the addition of 3 g. of potassium permanganate an exothermic reaction ensued and carbon dioxide was evolved. The reaction mixture was heated on the steam-cone for ten minutes and a solution of sodium bisulfite was added. The crystalline precipitate which separated was collected on a filter, dissolved in 1 *N* potassium hydroxide and treated with Norite. After acidification, the precipitate which formed was separated and recrystallized from benzene–petroleum ether to give 0.1 g. of product melting at 116.6°. Melting point (lit.[28] m.p. 116°), analysis and infrared absorption spectrum show the material to be β-benzoylpropionic acid (V). The infrared absorption spectrum with bands at 2.91, 5.84, 5.90 and 6.24 μ indicated the presence of a carboxylic acid and a phenyl ketone grouping.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.7; neut. equiv., 178. Found: C, 66.9, 67.1; H, 5.7, 5.7; neut. equiv., 181, 183.

2-Phenyltetrahydropyran (III).—A 12-g. sample of 2-phenyl-3,4-dihydro-2H-pyran in 30 ml. of ether was hydrogenated over 5 g. of Raney nickel at 40 p.s.i.g. for 24 hours at room temperature. Distillation gave 10.5 g. of 2-phenyltetrahydropyran boiling at 105–106° (10 mm.), n^{20}_{D} 1.5273, d^{20} 1.0145. The physical constants given by R. Paul[2b] are: 111–112° (10 mm.), n^{20}_{D} 1.53191, sp. gr.$^{15}_{20}$ 1.020.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.45; H, 8.70. Found: C, 81.23, 81.27; H, 8.76, 8.72.

2-*n*-Butyltetrahydropyran.—Fifteen grams of 2-*n*-butyl-3,4-dihydro-2H-pyran, whose analysis indicated it to contain some acrolein dimer, was hydrogenated in ethanol over Raney nickel at 1500 p.s.i. and room temperature as a means of purification. Distillation of the product gave besides 3 g. of 2-tetrahydropyranmethanol (from acrolein dimer) b.p. 80° (14 mm.), 11 g. of 2-*n*-butyltetrahydropyran boiling at 63–65° (14 mm.), n^{20}_{D} 1.4368. R. Paul[2a] records the physical constants as b.p. 64° (14 mm.), n^{21}_{D} 1.4382. 2-*n*-Butyltetrahydropyran prepared from 2-bromotetrahydropyran *via* the Grignard reaction according to the method of Paul[2a] had the following properties: b.p. 63–64° (14 mm.), n^{20}_{D} 1.4353. The infrared absorption spectra of the two samples of 2-*n*-butyltetrahydropyran (Fig. 1) were identical.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.73. Found: C, 75.66, 75.53; H, 12.62, 12.66.

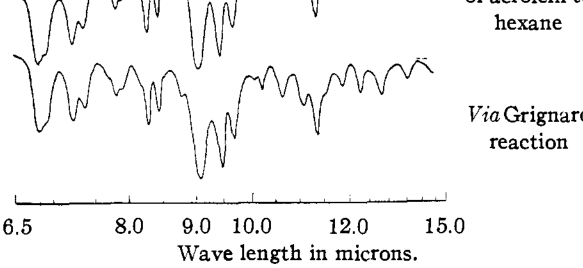

Fig. 1.—Infrared absorption spectra of 2-*n*-butyltetrahydropyrans (tracings).

Derivatives of 2,2-Dimethyl-3,4-dihydro-2H-pyran. A. 2,2-Dimethyltetrahydropyran.—A solution of 38 g. of 2,2-dimethyl-3,4-dihydro-2H-pyran in petroleum ether was hydrogenated over Raney nickel at 1400 p.s.i.g. and 75° for 16 hours. Distillation gave 36 g. of 2,2-dimethyltetrahydropyran boiling at 118–120°, n^{20}_{D} 1.4300.

Anal. Calcd. for $C_7H_{14}O$: C, 73.64; H, 12.36. Found: C, 73.83, 74.14; H, 11.73, 11.78.

B. 2,6-Dibromo-2-methylhexane (X).—2,2-Dimethyltetrahydropyran (IX), 21 g., was treated with 61 g. of hydrogen bromide at 70° for two hours. After release of the excess hydrogen bromide, the product was taken up in ether and extracted quickly with cold aqueous sodium bicarbonate. The ether solution was dried and distilled. There was obtained 26 g. of 2,6-dibromo-2-methylhexane boiling at 85–86° (0.5 mm.), n^{20}_{D} 1.5060.

Anal. Calcd. for $C_7H_{14}Br_2$: Br, 61.95. Found: Br, 60.7, 60.4.

A sample of the dibromide was allowed to stand for 30 minutes in 0.5 *N* alcoholic sodium hydroxide at room temperature. A Volhard titration of the bromide ion content gave a value of 26.2%; theory for one bromine, 20.9%.

C. Dehydrobromination.—After adding one drop of concentrated hydrobromic acid to 18 g. of 2,6-dibromo-2-methyl-2-hexane, the mixture was heated at 190° for 30 minutes. Upon distillation, there was obtained 7.1 g. of bromoölefin boiling at 104–109° (100 mm.), n^{20}_{D} 1.4475.

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(25) T. Wagner-Jauregg and E. Helmert, *Ber.*, **71B**, 2535 (1938).

(26) Since this paper was submitted for publication, there has come to our attention a paper by K. Alder, M. Schumacher and O. Wolff (*Ann.*, **570**, 230 (1950)) in which the reaction of sorbyl chloride and acrylyl chloride was reinvestigated and found to give *cis* as well as *meta*-type addition.

(27) L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, 2nd ed., John Wiley and Sons, Inc., 1941, p. 82.

(28) Fittig and Leoni, *Ann.*, **256**, 78 (1890).

Anal. Calcd. for $C_7H_{13}Br$: Br, 45.1; bromine no., 90.2 g. Br/100 g. Found: Br, 45.5, 45.7; bromine no., 82.2, 82.4 g. Br/100 g.

The infrared absorption spectrum indicated the presence of $R_2C{=}CH_2$ and $RCH{=}CR_2$ groupings but not the $RCH{=}CH_2$ grouping indicating that the product was a mixture of 6-bromo-2-methyl-1- (and 2)-hexene (XI).

2,5-Dimethyl-2-phenyltetrahydropyran.—A 19-g. sample of 2,5-dimethyl-2-phenyl-3,4-dihydro-2H-pyran was hydrogenated over Raney nickel at 25 p.s.i.g. and room temperature. Distillation gave 11.5 g. of 2,5-dimethyl-2-phenyltetrahydropyran boiling at 60–61° (1 mm.), $n^{20}D$ 1.5270, d^{20} 1.0083.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.07; H, 8.41. Found: C, 81.77, 81.69; H, 8.71, 8.71.

3-Methyl-5-hydroxy-5-phenylhexanal.—A mixture of 58 g. of 2,4-dimethyl-2-phenyl-3,4-dihydro-2H-pyran, 116 g. of 10% sulfuric acid and 200 ml. of dioxane was heated on the steam-cone for two hours and then allowed to stand at room temperature overnight. An oil layer was separated and the aqueous phase was extracted with petroleum ether. The combined oil and petroleum ether extract was dried and distilled to give 23.5 g. (36.8% yield) of 3-methyl-5-hydroxy-5-phenylhexanal boiling at 115–120° (0.3 mm.), $n^{20}D$ 1.4290.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 76.24, 76.11; H, 8.73, 8.80.

The infrared absorption spectrum showed bands at 2.95 μ (–OH), 5.83 μ (–CHO) and 6.23 μ ($-C_6H_5$).

EMERYVILLE, CALIF. RECEIVED MARCH 12, 1951

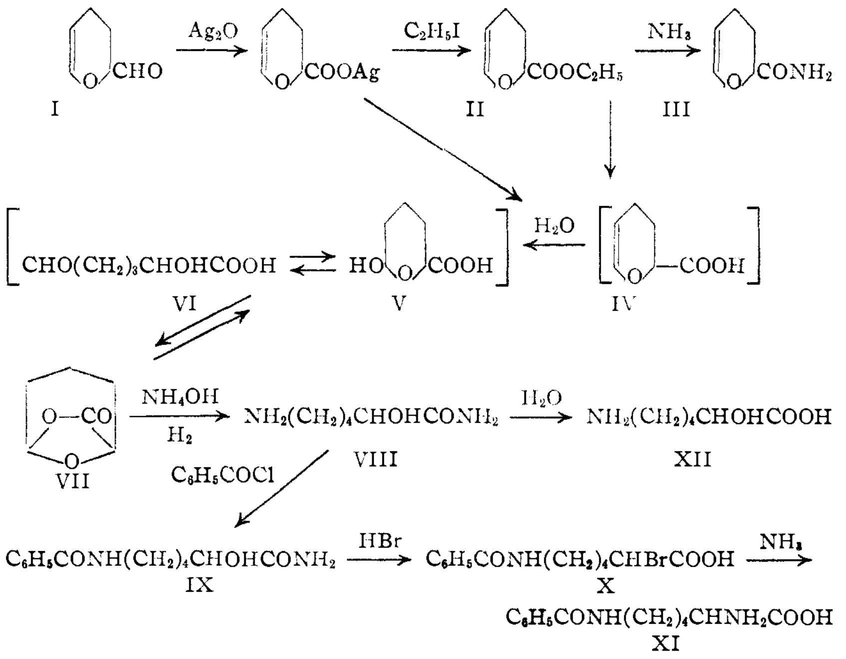
[CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY]

Reactions of Acrolein and Related Compounds. IV. Preparation of a New Lactone, 7-Oxo-6,8-dioxabicyclo[3.2.1]octane from Acrolein Dimer, and Its Conversion to Lysine

BY RICHARD R. WHETSTONE AND SEAVER A. BALLARD

dl-N$^\epsilon$-Benzoyllysine was prepared from acrolein dimer by a seven-step process. The preparation and properties of 7-oxo-6,8-dioxabicyclo[3.2.1]octane, a novel lactone of a carboxyhemiacetal, are described.

The many published syntheses of lysine have invariably required lengthening of a chain of less than six carbon atoms, introduction of one or more functional groups into a six-carbon compound or a combination of the two. Acrolein dimer (3,4-dihydro-2H-pyran-2-carboxaldehyde) therefore appears to be unique as a starting material in that, through the facile opening of the dihydropyran ring, it contains three existing or potential functional groups in the requisite 1,2,6-positions of a six-carbon chain. The synthesis of lysine from acrolein dimer by the stepwise transformation of these functional groups has been accomplished as shown in the diagram.



The oxidation of acrolein dimer (I) with silver oxide in aqueous solution to the corresponding acid (IV) isolated in low yield as the sodium salt was described by Sherlin, *et al.*[1] This procedure has been greatly improved by the use of dry silver oxide in ether or benzene; by reaction of the resulting crude silver salt with ethyl iodide, ethyl 3,4-dihydro-2H-pyran-2-carboxylate (II) was obtained in 71.5% yield from the dimer. Oxidation of acrolein dimer may be accomplished also *via* the Tishchenko reaction using aluminum isopropoxide as catalyst[2]; this reaction will not be described in this paper.

Hydrolysis of the ethyl ester (II) of the dihydropyran-2-carboxylic acid was readily accomplished by aqueous sodium hydroxide at room temperature; the reactivity of the ester to bases was also shown by the easy conversion to the amide (III) by mild warming with aqueous ammonia. Preliminary experiments indicated the difficulty of isolating the free acid (IV) and consequently acidification of the ester hydrolysis product with aqueous hydrochloric acid was carried out under conditions favoring hydration or hydrolytic cleavage of the dihydropyran ring or both. Acid solutions prepared in this manner or by treatment of a suspension of the silver salt of the dihydropyran acid with hydrochloric acid responded to reagents for the carbonyl group indicating that hydration or

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[1] S. M. Sherlin, A. Y. Berlin, T. A. Serebrennikova and F. E. Rabinovitch, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 22 (1938).

[2] Tishchenko, *J. Russ. Phys. Chem. Soc.*, **38**, 355, 482 (1906); *Chem. Zentr.*, **77**, II, 1309, 1552 (1906).