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# ON THE MECHANISM AND SYNTHETIC APPLICATIONS OF THE THERMAL AND ALKALINE DEGRADATION OF C-18 CASTOR OIL

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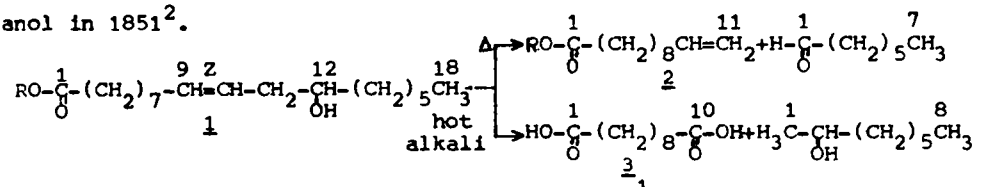
Abstract: The C-18 backbone of castor oil fragments, thermally to C-11 + C-7 by a $\pi^2s + \sigma^2s + \sigma^2s$ process and with hot alkali to C-10 + C-8 via unique sequence involving a primary reaction which is associated with three different types of redox systems as well as with uncoupled oxidation, the overall change amounting to a milieu of hydride transfer, $\pi$-migration, retro-Michael, retro-aldol, Meerwein-Pondorff-Verley as well as Cannizzaro type of reactions. These findings which constitute the core of the present work, are of significance, not only with respect to the understanding of two of the most important reactions of castor oil, but also in the utilization of this knowledge to channelize and optimize the products desired. Further, they add a distinct facet to mechanistic organic chemistry. Convincing evidence for the concerted nature of the C-18 ⟶ C-11 + C-7 change of castor oil is the clean transformation of methyl 12-hydroxy octadec 9-ynoate to the novel and useful allenic ester, methyl undeca 9,10-dienoate. Model studies with diversely $\alpha$-substituted $\gamma\delta$-unsaturated alcohols have shown that the $\pi^2s + \sigma^2s + \sigma^2s$ (retro-ene) process is assisted by a $C_\beta \longleftarrow C_\alpha$ polarization. The utility of the retro-ene reaction of $\gamma\delta$-unsaturated alcohols has been demonstrated with a novel procedure for the PhCHO ⟶ PhCOD change. The mechanism proposed in the present work for the C-18 ⟶ C-10 + C-8 change of castor oil with hot alkali provides a rationale for the formation of products at diverse redox levels. In the present work, the mechanism of the complex processes associated with the hot alkali fragmentation of castor oil has been probed using "castor soap", a standard recipe for which has been developed. Neat castor soap decomposes above 240° to give, hydrogen gas (!), 2-octanol (49%), 2-octanone (24%) and sebacic acid (12%). A very noteworthy finding was that the course of the above can be changed by the addition of external redox acceptors whereby the formation of 2-octanol and hydrogen are suppressed. Thus, non-enolizable ketones are reduced with castor soap [tetraphenylcyclopentadienone ⟶ tetraphenylcyclopentadiene (12%) + tetraphenylcyclopenteneone (35%); fluorenone ⟶ fluorene (34%); benzophenone ⟶ benzhydrol (44%)], hydrazones are converted to hydrocarbons [fluorenone hydrazone ⟶ fluorene (70%); benzophenone hydrazone ⟶ diphenylmethane (50%)] and, even with calculated quantities of castor soap, amounting to the required 6e transfer, excellent yields (81-95%) of aromatic amines were obtained from a variety of aromatic nitro compounds. The easily available castor soap has good practical potential. Additionally, the delineation of the multifaceted pathways associated with the castor oil ⟶ sebacic acid change with hot alkali could be used to advantage to optimize conditions relating to products at diverse redox

levels, the redox partners could be changed and the theme of co-existence of several redox systems could be transplanted to other substrates.

The rupture of the C-18 backbone of castor oil, thermally under neutral conditions to C-11 + C-7 on the one hand, and with hot alkali to C-10 + C-8 on the other, is of significance, since, almost all of the very many synthons that owe their genesis to this unusual, yet abundant natural product and which are extensively used for the synthesis of a wide and varied range of compounds, arise from this fragmentation. In spite of their obvious importance, these scission pathways have not been examined in any detail. Having had the opportunity to extensively use synthons derived from castor oil for the preparation of prostaglandins and insect sex-pheromones[1], over the last decade, it was felt most appropriate to report our studies pertaining to the mechanisms of the fragmentation of castor oil. In this paper, related information pertaining to the above mentioned fragmentations have been augmented with that from our own studies to present a comprehensive picture, which from mechanistic as well as practical view points should be useful.

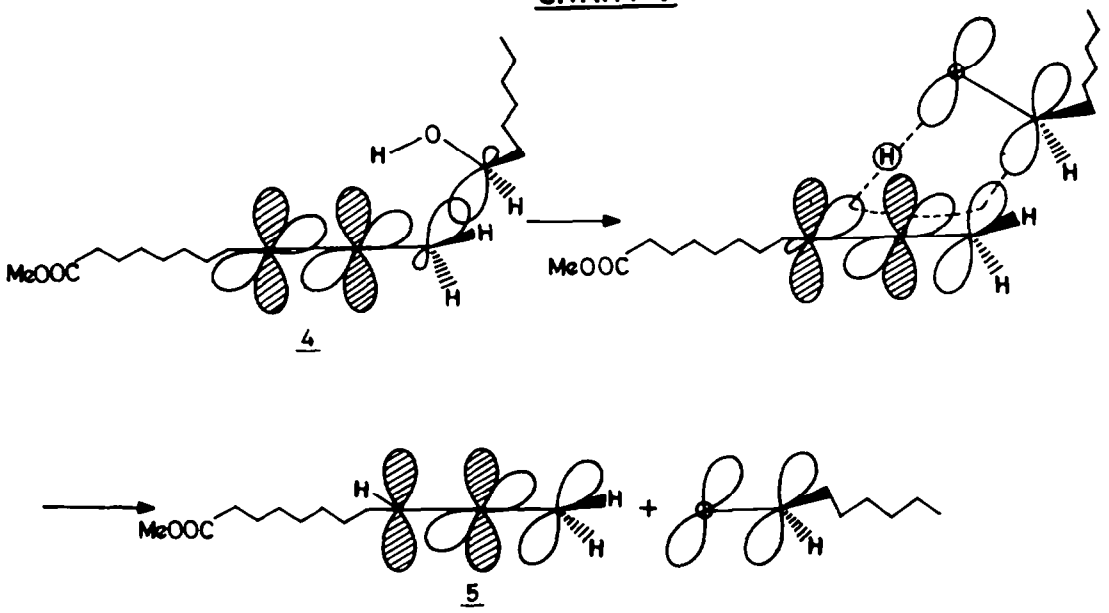
The thermal fragmentation of castor oil to 10-undecenoic acid and heptaldehyde proceeds *via* a concerted $\pi^2s + \sigma^2s + \sigma^2s$ process; in contrast, that with hot alkali leading to sebacic acid, is complex, with the course of the reaction sensitive to a variety of factors, since, the overall process involves a mileu of, hydride transfer, $\pi$ migration, retro-Michael, retro-aldol, Meerwein-Pondorf-Verley reduction and Cannizzaro reaction.

The thermal rupture of castor oil (1) to undecenoic acid (2) and heptaldehyde was discovered in 1827 and that with hot alkali to sebacic acid (3) and 2-octanol in 1851[2].




In the course of the transformation 1 to $PGF_1\alpha$[1], we had effected the transformation of about seventy litres of castor oil to 2, and developed a reliable recipe for this change. The mechanism of this fragmentation was explored with the primary objective of making it more efficient. Although the 1 ⟶ 2 +heptaldehyde change can be rationalized as a $\pi^2s + \sigma^2s + \sigma^2s$ (retro-ene)[3] process, it was felt that it was desirable to establish this in such a complex substrate as 1[4]. The thermal fragmentation of methyl 12-hydroxy octadec 9-ynoate (4) was therefore examined. The "retro-ene" pathway would give rise to the novel allenic ester 5. On the other hand, fragmentation by non-concerted modes would give mixtures, largely comprising of acetylenic products. An added attraction is that, thus far, a $\pi^2s + \sigma^2s + \sigma^2s$ pathway has not been demonstrated for $\gamma\delta$-unsaturated acetylenic alcohols. In the event, methyl 12-hydroxy octadec 9-ynoate (4), prepared from castor oil in 81% overall yields by a somewhat modified procedure, on thermolysis underwent smooth fragmentation to the expected allenic ester (5) in 71% yield. Careful analysis of the reaction mixture failed to yield any acetylenic fragmentation products. A comparison of the retro-ene processes involving the olefinic system, methyl ricinoleate (1) and the acetylenic, methyl 12-hydroxy octadec 9-ynoate (4) shows that the latter is a better substrate for the scission. This may be due to the operation of a relaxed transition state for the retro-ene reaction in the case of $\gamma\delta$--acetylenic alcohols (CHART I) or may be as well because of diminished tendency for elimination, which is a major competing pathway in the castor oil pyrolysis (*vide infra*).

## CHART I

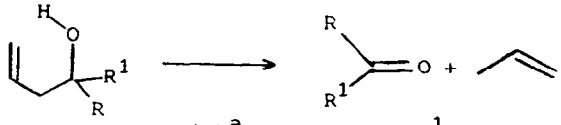


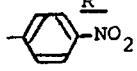
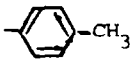

4 5

The 4 ⟶ 5 change has been taken advantage of, for the transformation of terminal acetylenes to higher allenes via 2-hydroxy ethylation with ethylene oxide followed by thermolysis. Further, compound 5 has been transformed to methyl 11-oxo(E) undecenoate, a useful synthon for prostaglandins and insect-sex pheromones, by hydroboration-oxidation[5].

With the primary objective of effecting the 1 ⟶ 2 change, under the mildest possible conditions, and in good yields, the influence of the α-substituent on the retro-ene fragmentation was then studied[6]. The model substrates prepared from the appropriate carbonyl compounds by allyl Grignard additions, were thermolysed under conditions of the 1 ⟶ 2 change and the ease of scission assessed in terms of the isolated yields of the aldehydes. The results are presented in TABLE I. The variation in the yields of scission products obtained, as a function of the α-substituent, clearly indicates that $\pi^2s + \sigma^2s + \sigma^2s$ processes

TABLE I. Thermolysis of γ,δ-unsaturated alcohols at 400°C for 1 hr



| R | $R^1$ | Isolated yield(%)[a] | R | $R^1$ | Isolated yield(%)[a] |
|---|---|---|---|---|---|
| -H | -Ph | 39 | -H |  | 18[b] |
| -H |  | 71 | $-CH_3$ | -Ph | 57 |

a. based on crystalline semicarbazones, not taking into account recovered starting materials, b. yield of crystalline aldehyde.

are associated with a $C_\beta \longleftarrow C_\alpha$ polarisation in the transition state and reflects the importance of the scission of this bond over C-H bond formation. This finding is in agreement with the observation that the transition state pertaining to the reverse of the process, namely, the ene reaction ($\pi^2s + \pi^2s + \sigma^2s$) is characterised by the importance of the $C_\beta - C_\alpha$ bond formation[7]. The yields, presented in Table I, are not the best possible, since, part of the terminal unsubstituted π system is not available for the fragmentation due to side reactions. This can be avoided by using the crotyl system (vide infra).

The desired α-substitution of the γδ-unsaturated alcohol unit can be brought about by PCC oxidation followed by appropriate addition to the resulting carbonyl function. Thus, phenyl(E)-2 butenyl methanol was transformed, by PCC oxidation and $NaBD_4$ treatment to phenyl deutero E-2 butenyl methanol with an overall yield of 80%. The latter on thermolysis gave a 93% yield of PhCOD. To translate such a strategy to the 1 ⟶ 2 change, compound 1 (R=Me) was readily oxidised to methyl 12-oxo octadec(Z)-9-enoate (6) and then transformed to the diol 7 with PhMgBr. It was anticipated that compound 7, under conditions of the 1 ⟶ 2 change, would undergo ready (Cf. TABLE I) fragmentation to 1,1-diphenyl undeca 1,10-diene (8), a key synthon related to prostaglandins and insect sex pheromones[1] and phenyl hexyl ketone. In the event however, the only product that could be isolated was 1,1,12-triphenyl octadec(E,E)-1,9,11-triene (9) arising from elimination.

The transformation of castor oil to sebacic acid in excellent yields is a unique reaction. A careful survey has shown that there appears only one example, reported in the form of an obscure communication[8] wherein an, γδ-unsaturated alcohol unit is similarly cleaved. This is the reported transformation of isopulegol (3-methyl, 6-isopropenyl cyclohexanol) to 3-methyl cyclohexanol with hot alkali. The major problem that faced us pertaining to the understanding of the castor oil ⟶ sebacic acid change was to coherently explain the very many experimental observations in the literature wherein the conditions were worked out for the optimum yields of substrates at diverse redox levels. The multi-facetted nature of this change is illustrated in Table II, which endeavours to present, to the best of our knowledge, the currently available information on this reaction.

TABLE II. Reaction of castor oil with hot alkali

| No. | Substrate | Per mole of substrate: NaOH | $H_2O$ | Control/ Catalyst | Temp. °C | Product(s) | Yld % | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | 1(R=H) | 7.5 | 6.6 | - | 200 | $HO(CH_2)_9COOH$ + $Ac\text{-}(CH_2)_5CH_3$ | 14<br>43 | 9 |
| 2 | 1(R=glyceride) | 6 | 4 | - | 180 | $HO(CH_2)_9COOH$ | 40 | 10 |
| 3 | 1(R=glyceride) | 12 | 26 | CdO(0.2mol) | 275 | $HOOC(CH_2)_8COOH$ | 84 | 11 |
| 4 | 1(R=glyceride) | 2 | 2.6 | - | 230 | $CH_3CH(OH)\text{-}(CH_2)_5CH_3$ | 25 | 12 |
| 5 | 1(R=Me) | 4 | 4 | $Pb_3O_4$ (0.02 mol) | 250 | $HOOC(CH_2)_8COOH$ | 70 | 13 |
| 6 | 1(R=H) | 2.2 | 15 | - | 202 | $HO(CH_2)_9\text{-}COOH$ + $HOOC(CH_2)_8COOH$ | 23<br>37 | 13 |
| 7 | 1(R=H) | 7.5 | 5 | $Ac(CH_2)_5CH_3$ (3.8 mol) | 184 | $HO(CH_2)_9COOH$ + $HOOC(CH_2)_8COOH$ | 19<br>67 | 13 |
| 8 | 1(R=H) | 7.5 | 5 | $CH_3CH(OH)\text{-}(CH_2)_5CH_3$ (3.75 mol) | 183 | $HO(CH_2)_9COOH$ + $HOOC(CH_2)_8COOH$ | 80<br>11 | 13 |

In addition to our own investigations pertaining to this reaction, we have confirmed most of the observations presented in Table II. The yields of products are hardly affected whether the reactions are conducted in nitrogen atmosphere or without. Remarkably, there is a sharp change in the course of the transformation around 240°C where hydrogen gas evolution takes place copiously. We have also ruled out the intermediacy of epoxides by model studies.

In view of the divergence in reaction conditions and reagents, it was felt that a well defined substrate would be more suitable for further studies. Such a substance was fortunately available in the form of what is called as "castor soap"

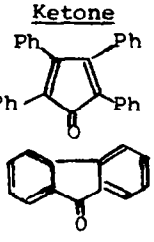
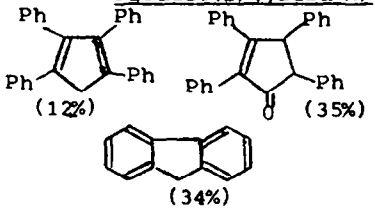
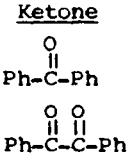
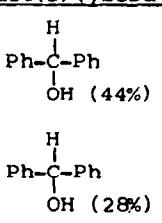
which was prepared originally by Adams and Marvel and whose pyrolysis provided a standard recipe' for the preparation of the industrially important 2-octanol, although in a modest yield of 25%[12].

"Castor Soap" was readily prepared by the addition of 2 moles of NaOH per mole of ricinoleic acid as an aqueous solution ($NaOH:H_2O::5:3$) to stirred castor oil. An ivory coloured hard soap is formed soon with evolution of considerable heat. It was found that such a soap is not formed when only one equivalent of NaOH was used. Two hundred and fifty gram lots of castor-soap were prepared, pulverised and used in all experiments. Interestingly, the pH of a molar solution of this material was found to be ~ 10. It is possible that the extra mole of hydroxide has been used to a considerable extent via reaction with the hydroxyl functions present either in the ricinoleic acid or glycerol.

The castor-soap melts around 220° and rapidly decomposes at 240° with vigorous evolution of hydrogen gas ! One hundred grams of castor-soap was thermolysed, generally according to the procedure of Adams and Marvel[12] for 7 hr and distilled. The distillate consisted of largely a mixture of 2-octanol and 2-octanone in the ratio 2:1. The combined yield was a remarkable 73%, vastly superior to that reported in organic synthesis ![12] The boiling points of 2-octanol and 2-octanone being respectively, 175°C and 173°C, they cannot be easily separated. From the practical view point, the total distillate is best transformed either by PCC oxidation to 2-octanone or by borohydride reduction to 2-octanol. Thus, castor soap is a very superior starting material for either 2-octanone or 2-octanol. The residue on work-up gave 12% yield of sebacic acid. The yield was poor and was so anticipated on the basis of experimental conditions (vide infra).

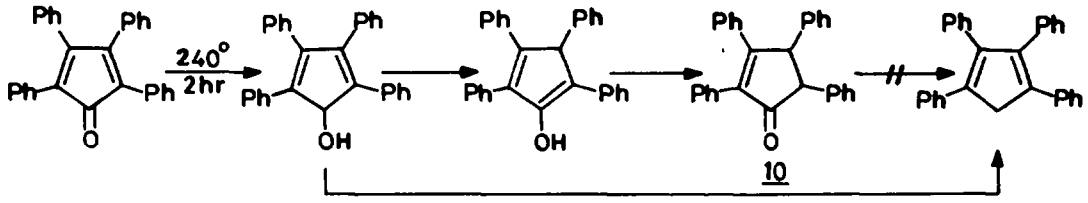
A very noteworthy finding was that the course of the above change can be completely altered by the addition of external redox acceptors. Thus, on thermolysis of castor soap with non-enolizable ketones, the formation of 2-octanol and the evolution of hydrogen are suppressed leading to the isolation of reduced ketones. In these studies, 1 mmol of the external acceptor was mixed with 10g of castor-soap (~ 22 mmole of hydride equivalent, assuming that the primary step is solely and completely involved in the hydride transfer) and held at 240° for 2 hr. The results are presented in TABLE III.

TABLE III. Reduction of non-enolizable ketones with castor soap at 240° for 2 hr.

| Ketone | Product(s)(yield %) | Ketone | Product(s)(yield %) |
|---|---|---|---|
|  |  (12%) (35%) (34%) |  |  (44%) (28%) |

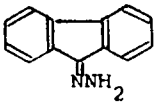
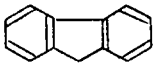
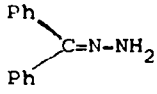
Tetracyclone gave not only 35% of the expected enone 10, but, surprisingly, also a 12% yield of tetraphenyl cyclopentadiene. The latter is not easy to come-by and perhaps the only rational procedure for the compound is the reduction of tetracyclone with LAH + $AlCl_3$.[14] Blank experiments showed that the enone 10 is not a precursor to the hydrocarbon (CHART II). Fluorenone gave a 34% fluorene; fluorenol was not present. On the other hand, in the case of benzophenone the reduction stopped at the first hydride acceptance stage, leading to a 44% yield of benzhydrol. Benzil, interestingly, gave a 28% yield of benzhydrol, whose formation is rationalized on the basis of benzilic acid type rearrangement, fragmentation to benzophenone and reduction.

## CHART II



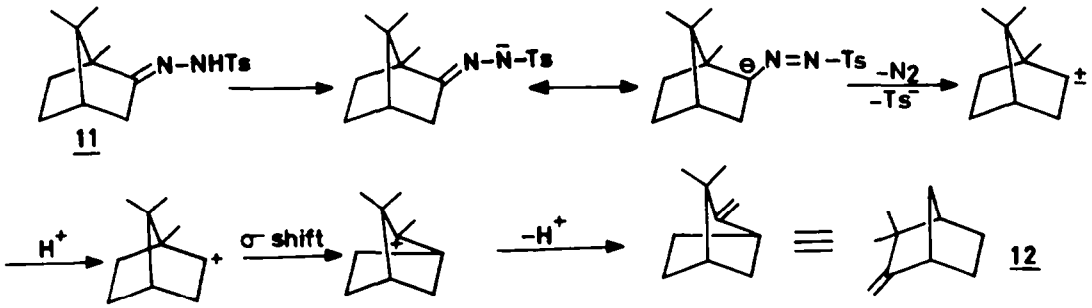

The castor soap was found to be a very good medium for Wolff-Kishner type of reduction. Thus, under conditions outlined above, fluorenone hydrazone gave a 70% yield of fluorene and benzophenone hydrazone a 50% yield of diphenyl methane (TABLE IV). A remarkable reaction brought about with castor soap is the camphor

TABLE IV. Reduction of hydrazones with castor soap at 240°C for 4 hr

| Hydrazone | Product (yield %) | Hydrazone | Product (yield %) |
|---|---|---|---|
|  |  (70%) |  | $PhCH_2Ph$ (50%) |

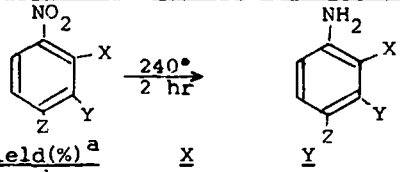
tosylhydrazone (11) ⟶ camphene (12) change, accomplished in 80% yields by the thermolysis of 20 mmoles of 11 with 20g of castor soap, under conditions described earlier. The key intermediate in the change must be bornane 2-cation, arising from either carbenic or diazonium precursors (CHART III).

## CHART III : The generation of carbenic intermediate with "castor-soap" at 240° for 3 hr.




The most effective redox acceptor has been found to be the aromatic nitro function. Thus, even with calculated amounts of castor-soap, amounting to the required 6 electron transfer, excellent yields of amino compounds were obtained from a variety of aromatic nitro compounds (TABLE V).

TABLE V. Reduction of aromatic nitro compounds with castor soap




| X | Y | Z | Yield(%)[a] | X | Y | Z | Yield(%)[a] |
|---|---|---|---|---|---|---|---|
| H | H | H | 56[b] | $NH_2$ | H | H | 93 |
| $CH_3$ | H | H | 81 | H | H | Cl | 88 |
| H | $CH_3$ | H | 95 | $NO_2$ | H | H | 91[c] |
| H | H | $CH_3$ | 84 | | | | |

a. Isolated as crystalline picrates; b. Isolated as aniline; c. Product was o-phenylene diamine.

In sum, we feel that the easily available castor-soap has good practical potential in the reduction of a variety of substrates. From the above account,

it is clear that the castor oil ⟶ sebacic acid change involves intermediates, which, as a function of temperature and reaction conditions, could further influence the course of the reaction.

We feel that the castor oil ⟶ sebacic acid change could be best analysed in terms of three events, namely I. a primary reaction, II. the operation of redox systems A,B and C and III, uncoupled oxidations.

The primary reaction in the castor oil ⟶ sebacic acid change is envisaged to involve the rupture of the ricinoleic acid (1) unit to 2-octanone and 10-oxo decanoic acid (13), *via* sequence, loss of elements of hydride ion from the conjugate base of the ricinoleate leading to, 12-oxo octadec (Z) 9-enoate (6) followed by ready isomerisation to the α,β unsaturated ketone, 12-oxo octadec (E) 10-enoate (14), Michael addition and retro aldol reaction. In accordance with this, it has been reported that 12-oxo octadec(Z) 9-enoic acid (6) on treatment with very dilute NaOH (0.03N) at comparatively low temperature (100°C) gives 2-octanone in 36% yield[15]. A very important observation is that, none of the expected 10-oxo decanoic acid (13) could be isolated, since, because of its highly sensitive nature, it underwent polymerization. A very pertinent fact is that, in sharp contrast to its fugitive nature at 100°, 10-oxo decanoic acid independently prepared from 10-undecenoic acid is transformed to sebacic acid at 240° !.[15]

The most fascinating aspect of the castor oil ⟶ sebacic acid change is the controls exerted by diverse redox systems. These can be influenced by concentration of alkali present and the temperature at which the reaction is carried out. Thus, when the redox systems are not effective, such as, at low NaOH concentration and low temperature, degradation stops at the first stage leading to the primary fragmentation products 2-octanone and 10-oxo decanoate(13), as was found in the model system 6. However, in the case of castor oil or ricinoleates, the primary stage is subject to a prior oxidation with hydride transfer. From the information thus far available, it appears that the conditions under which this can be brought about - higher alkali concentration and temperature above 180°C - redox systems do operate, thus resulting in additional products.

Sebacic acid arises, when externally added controls and oxidants are not present, by uncoupled oxidations, which require a temperature in the range 240°C and a high hydroxide concentration. Around 180°C, the primary reaction becomes possible leading to 10-oxo decanoate and 2-octanone, both of which can take part in the first steps of the primary reaction, namely, the hydride transfer. The isolation of only 10-hydroxy decanoic acid and 2 octanone under such conditions (Table II, Nos. 1,2) show that 2-octanone does not enter the redox system at this stage. The reaction of geraniol (3,7-dimethyl(Z)-2,6-dienol) with alkali at 150°C leading to 6-hydroxy 2-methyl 2-heptene and acetaldehyde[16] can be rationalized *via* pathways precisely described for the ricinoleic acid ⟶ 10 hydroxy decanoate + 2-octanone change at 180°C. Presumably, the acetaldehyde formed under these conditions is too unstable to be a partner in the redox system and consequently the acceptor becomes the other product from the primary reaction, namely, 6-oxo 2-methyl 2-heptene. This view finds support in the observation that the fragmentation of the allyl alcohol, 6-hydroxy 5-ethyl(E)-dec 4-ene with hot alkali at 200° leads to 4-octanone and n-butanol, the latter arising from redox reaction involving the primary fragmentation product, butyraldehyde. At 240°C however, the products isolated are 4-octanol, butyric acid and hydrogen, arising from diversion of butyraldehyde *via* uncoupled processes[9]. It may be noted that at temperature of 230° with similar alkali concentration (Table II, No.4), 2-octanone enter the redox system leading to 2-octanol, since the 10-oxo decanoate which can be anticipated to be a better redox acceptor compared to 2-octanone is converted preferentially to sebacic acid *via* uncoupled oxidations (*vide infra*).

Interesting events take place when the reaction is done at 240° at low alkali concentrations, which is characterized by a low yield of sebacic acid and a modest yield of 2-octanol. The uncoupled oxidation of 10-oxo decanoic acid which is dependent on high alkali concentration, is, in this case not efficient and a substantial portion of 13 is destroyed by polymerization. On the other hand, 2-octanone enters and redox system leading to 2-octanol. All our experiments with castor-soap were characterized by a highly efficient hydride transfer and a low yield of sebacic acid. The course of the alkaline cleavage, with added controls 2-octanone and 2-octanol, are very instructive (Table II, Nos. 7,8) and provides convicning evidence for their participation in the redox systems.

It is thus possible to discern the operation of three types of redox systems in the alkaline cleavage of castor oil ⟶ sebacic acid:

A. The oxidation of ricinoleate to 12-oxo octadec(Z) 9-enoate coupled with the reduction of, either, 10-oxo decanoate or with 2-octanone, leading to, respectively, 10-hydroxy decanoate or 2-octanol.
B. The oxidation of 10-oxo decanoate to sebacic acid coupled with the reduction of 2-octanone.
C. The oxidation of 2-octanol to 2-octanone coupled with the reduction of 10-oxo decanoate to 10-hydroxy decanoate.

The systems described above are those involved in the castor oil ⟶ sebacic acid change. Our work on a variety of acceptors have demonstrated that a wide spectrum of acceptors and, perhaps equally well, donors, could be extraneously introduced into the system.

The third facet associated with the alkaline castor oil ⟶ sebacic acid change is the uncoupled oxidations that account for the hydrogen gas evolved in the process.

Weedon and co-workers[17] have extensively studied the transformation of a variety of hydroxyl containing substrates in hot alkali. Invariably these compounds are oxidized to the carbonyl compounds with release of hydrogen. A striking example of such change is the total degradation of 1,7-dihydroxy hept 3-ene to acetic acid, glutaric acid and hydrogen :[18]


It may be noted that the above substrate possesses a γδ -unsaturated alcohol moiety as in castor oil. However, the conditions of the reactions and the nature of the compounds were such that the progress was relentlessly towards uncoupled oxidation !

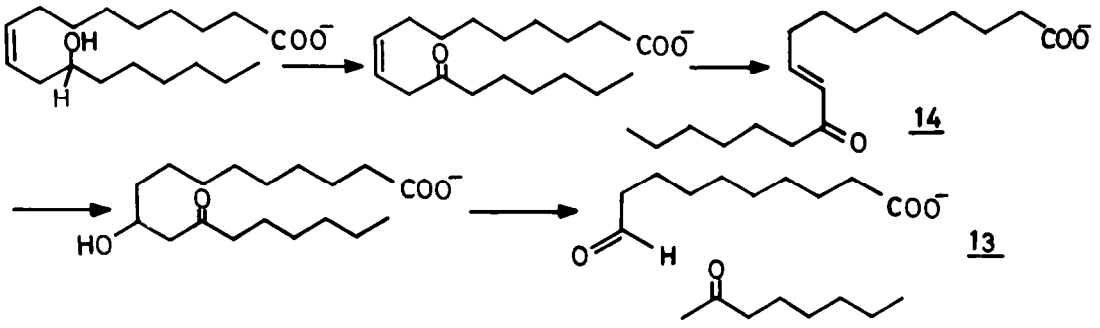
In the case of the castor oil⟶ sebacic acid change, in principle, three substrates, namely, ricinoleate (1), 10-oxo decanoate (13) and 2-octanol could be associated with the uncoupled oxidations leading to respectively 12 oxo octadec (Z) 9-enoate, sebacate and 2-octanone.

Thus, the spectrum of reactions associated with the transformation of castor oil to sebacic acid can be presented in an integrated manner as shown in CHART IV.

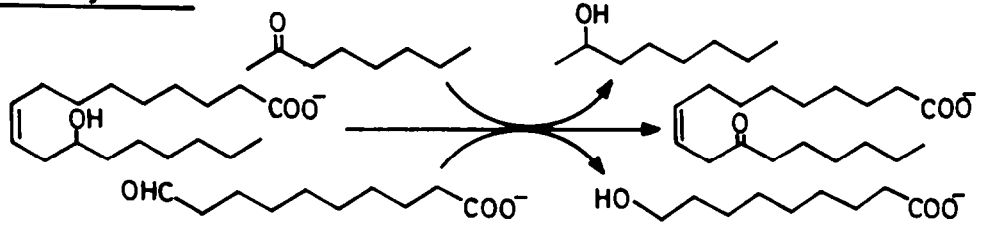
The present work has brought to focus, the multifacetted nature of the cleavage of castor oil under alkaline conditions. It appears that the benefits arising from the understanding of this transformation, as illustrated in CHART IV, should be considerable. Thus, the course of events could be further controlled to optimize yields, the cleavage could be achieved under milder conditions, the redox partners could be changed, the theme or co-existance of several redox systems could be transplanted in other substrates and efficient and inexpensive reagents could be developed on such an understanding. Parenthetically, we have

CHART IV: Thermal transformation of castor oil under basic environments.

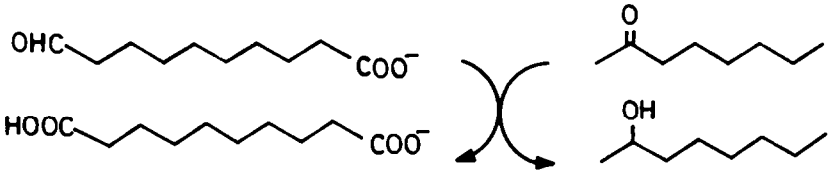
Primary reaction



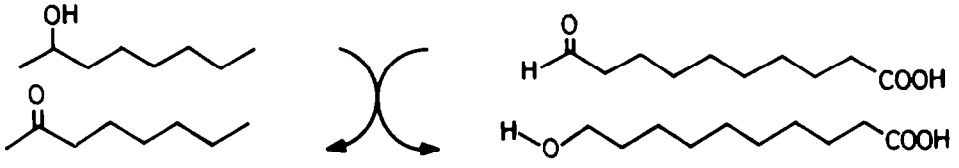

Redox system I



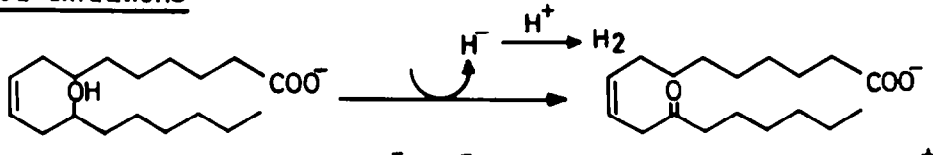

Redox system II

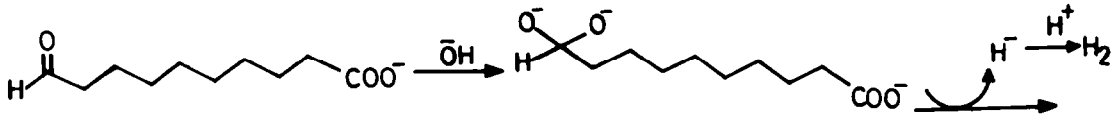


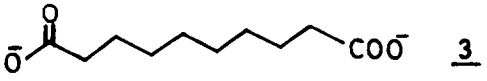

Redox system III

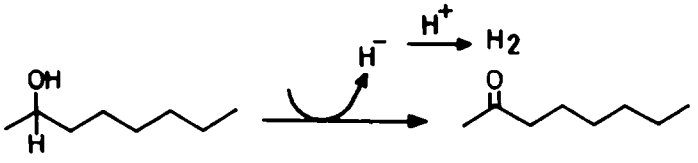



Uncoupled oxidations



recently used sebacic acid as an excellent source for insect sex pheromones and other synthons.[5]

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## EXPERIMENTAL

### Thermal fragmentation of methyl 12 hydroxy octadec(Z) 9-ynoate(4) to methyl 9,10-undecadienoate (5) and heptanal

Compound 4[19] was prepared as follows:

Bromine (40g, 0.25 mol) was added in a thin stream to well stirred and cooled (-30°C) solution of castor oil (70g, 0.075 mol) in EtOH (40 ml). The reaction mixture was allowed to attain rt, admixed with aqueous KOH (80g, 1.43 mol; 50 ml), refluxed for 10 hr, poured onto ice-water (500 ml), acidified with cold 5N $H_2SO_4$, left aside overnight, extracted with ether, dried, solvents evaporated, the resulting acid dissolved in dry MeOH (1000 ml), admixed with conc. $H_2SO_4$ (1 ml), refluxed for 4 hr., solvents evaporated, the residue poured onto ice-water (600 ml), extracted with ether (3x300 ml), washed with satd. $NaHCO_3$, brine, dried and evaporated to give 55.7g (81%) of 4, bp 130-135°/0.05 torr.

### Pyrolysis of 4

Under set up for distillation, 4 (25g, 0.08 mol) evenly supported on sand or glass wool (≈ 5g) was pyrolyzed for 0.5 hr using a luminous flame. The distillate (22g) on fractionation gave 5g (71%) of 5, bp 75-78°/0.07 torr and unchanged 4 (14g), bp 130-135°/0.05 torr. Calcd for $C_{12}H_{20}O_2$ (M.W. 196) C, 73.47; H, 10.2; Found C, 73.69; H, 9.87; ir: $\nu_{max}$(neat)(cm-1): 1950 (allene), 1740 (ester); nmr: $\delta$ ($CCl_4$): 2.15 (m, 4H, $-CH_2COOCH_3$, $=CH-CH_2-CH_2$), 3.5 (s, 3H, $COOCH_3$), 4.45 (qq, 2H, $H_2C=C=C-H$), 4.9 (m, 1H, $H_2C=C=C(H)CH_2$).

### Thermolytic studies of α-substituted γδ-unsaturated alcohols

The γδ-unsaturated alcohols were prepared by addition of allyl magnesium bromide to the appropriate carbonyl compounds by the following general procedure. To a well stirred solution of allyl magnesium bromide, prepared from 2.16g (0.09 mol) Mg and 9.168g (0.075 mol) of allyl bromide in ether (150 ml), was added, in drops, over 0.5 hr, keeping the temperature below 25°, a solution of 0.05 mol of the carbonyl compound in ether (50 ml). The reaction mixture was left stirred for 2 hr, the Grignard complex decomposed with satd. $NH_4Cl$, extracted with ether, washed with brine, dried ($MgSO_4$) and distilled.

Phenyl 2-propenyl carbinol: bp 65-67°/0.1 torr; yield 71.5%; Calcd. for $C_{10}H_{12}O$ (M.W. 148): C, 81.35; H, 8.1; Found C, 80.97; H, 8.34%; ir: $\nu_{max}$(neat)(cm-1): 3400 (OH), 1640 (double bond), 1600 (phenyl); nmr: $\delta$($CDCl_3$): 2.2 (br, t, 2H, allyl $CH_2$), 3.1 (br, 1H, -OH), 4.4 (t, 1H, tert. proton), 5.0 (br, d, 2H, $H_2C=C(H)-$), 6.5 (m, 1H, $H_2C=C(H-)$.

p-Toluyl 2-propenyl carbinol: bp 80-82°/0.15 torr; yield 65.8%; Calcd. for $C_{11}H_{14}O$ (Mol. Wt. 162): C, 81.48; H, 8.64; Found C, 81.51; H, 8.79%; ir: $\nu_{max}$ (neat)(cm-1): 3400 (OH), 1635 (double bond), 1610 (phenyl); nmr: $\delta$($CDCl_3$): 2.2(m, 5H, Ar-$CH_3$, allyl-$CH_2$), 3.1 (s, 1H, OH), 4.3 (t, 1H, tert. proton), 4.9 (br, d, 2H, $H_2C=C(H)-$), 5.6 (m, 1H, $H_2C=C(H)-$).

p-Nitrophenyl 2-propenyl carbinol: bp 55-60°/0.2 torr; yield 67%; ir: $\nu_{max}$(neat) cm-1: 3350(OH), 1540, 1340 ($NO_2$).

Phenyl, methyl, 2-propenyl carbinol: bp 62-64°/0.07 torr; yield 72.5%; Calcd. for $C_{11}H_{14}O$ (Mol. Wt. 162): C, 81.48; H, 8.64; Found C, 81.71; H, 8.49%; ir: $\nu_{max}$ (neat) $cm^{-1}$: 3440 (OH); nmr: $\delta$($CCl_4$): 1.5 (s, 3H, $-CH_3$), 2.2 (s, 1H, OH), 2.5 (t, 2H, allyl-$CH_2$), 5.0 (br, d, 2H, $H_2C=C(H)-$), 5.6 (br, $H_2C=C(H)-$). The allyl alcohols were evenly supported on glass-wool, admixed with few crystals of hydroquinone and held at 400°C for 1 hr. The results are presented in Table I.

### Ph-C(=O)-H ⟶ Ph-C(=O)-D by γδ-unsaturated alcohol fragmentation

a. Phenyl(E) 2-butenyl carbinol was prepared from crotyl magnesium bromide and benzaldehyde as described in the previous experiment for the related allyl series. bp. 55-58°/0.05 torr; yield 60%; Calcd. for $C_{11}H_{14}O$ (Mol. Wt. 162): C, 81.48; H, 8.64; Found C, 81.73; H, 8.23%; ir: $\nu_{max}$(neat) $cm^{-1}$: 3450 (OH); nmr: $\delta$($CCl_4$): 2.1-2.6 (m, 5H, $CH_3-CH=CH_2-$, allyl-$CH_2-$), 4.3 (t, 1H, tert. proton), 5.0 (m, 2H, $H_2C=C(H)-$), 5.6 (m, 1H, $H_2C=C(H)-$).

b. Phenyl E-2 butenyl ketone: To a well stirred suspension of PCC (6.45g, 0.03 mol) in $CH_2Cl_2$ (10 ml), at rt, was added, in drops, a solution of phenyl(E)-2 butenyl carbinol (3.23g, 0.02 mol) in $CH_2Cl_2$ (5 ml). The reaction mixture was left stirred at rt for 2 hr, admixed with ether (150 ml), passed through a small column of $MgSO_4$ and evaporated to give 2.746g (85.6%) of the ketone; ir: $\nu_{max}$ (neat) $cm^{-1}$: 1700 (CO).

c. Phenyl(E) 2-butenyl carbinol(D): To a stirred suspension of $NaBD_4$ (0.213g, 0.007 mol) in dry THF (20 ml), at rt, was added a solution of phenyl E-2 butenyl ketone (1.335g, 0.008 mol) in dry THF (10 ml). The reaction mixture was refluxed for 1 hr, excess reagent decomposed by addition of water, extracted with ether, washed with brine, dried ($MgSO_4$), solvents evaporated and the residue on distillation gave 1.215g (93%) of the deuterated alcohol, bp 110-115°/3 torr; ir: $\nu_{max}$ (neat) $cm^{-1}$: 3400 (OH), 2140 (C-D).

Benzaldehyde (D): Thermolysis of phenyl E-2 butenyl carbinol(D) as described previously gave 93.4% yield of PhCOD isolated as semicarbazone mp. 218-221°; ir: $\nu_{max}$(neat) $cm^{-1}$: 3640 (NH), 2210 (C-D), 1690 ($CONH_2$); ms:m/e: 164 ($M^+$). This yield is based on recovered starting material (~ 50%).

Attempted preparation of synthon, 1,1-diphenyl 1,10-undecadiene by γδ unsaturated alcohol fragmentation: Isolation of 1,1,12 triphenyl octadeca(E)(E)-1,9,11 triene(9)

a. Methyl 12-oxo oleate(6): A solution of methyl ricinoleate[1] (1) (6.24g; 0.02 mol) in dry $CH_2Cl_2$ (20 ml) was added, dropwise, at rt, to stirred Collins reagent [prepared from $CrO_3$ (12g, 0.12 mol) and pyridine: $CH_2Cl_2$::1:10, 220 ml], left stirred for 24 hr, decanted, the residue washed with dry $CH_2Cl_2$ (20 ml), the combined extracts washed with 5% sodium sulphite, 5% HCl, chilled water, dried ($MgSO_4$), solvents evaporated and the residue chromatographed on silica gel. Elution with benzene:EtOAc::85:15 gave 4.8g (84%) of 6, bp. 125°/0.05 torr; ir: $\nu_{max}$(neat) $cm^{-1}$: 1740 (Ester), 1715 (CO); nmr: δ ($CDCl_3$): 3.15 (d, J=5Hz, 2H, $=CH-CH_2-CO$), 3.65 (s, 3H, ester), 5.5 (t, J=5Hz, 2H olefin).

1,12-Dihydroxy 1,1,12-triphenyl octadec(Z) 9-ene(7)

To stirred PhMgBr [prepared from 1.0g Mg (0.04 mol) and 6.28g (0.04 mol)PhBr in ether (250 ml)] was added, over 0.5 hr, at 20°C, a solution of 6 (2.96g, 0.01 mol) in ether (50 ml). The mixture was left stirred for 15 hr, the Grignard complex decomposed with 2N $H_2SO_4$, extracted with ether, washed with satd. $NaHCO_3$, brine, dried ($MgSO_4$) and solvents evaporated to give 3.5g (78%) of 7 which was used as such in the following experiment. ir: $\nu_{max}$(neat) $cm^{-1}$: 3420 (OH).

1,1,12-Triphenyl octadeca (E)(E)-1,9,11 triene(9)

Thermolysis of 7 (2.5g, 0.005 mol) was carried out under conditions standardized for the 1 ⟶ 2 fragmentation[1]. There was practically no distillate. The residue was extracted with benzene, solvents evaporated and chromatographed on silica gel. Elution with hexane:benzene::20:80 gave 1.8g (78%) of the triene 9 as a viscous liquid, ir: $\nu_{max}$(neat)($cm^{-1}$): 1650, 790 (double bond), 1600 (Phenyl)

Preparation of Castor Soap:

To hand-stirred castor oil (190g, 0.2 mol) in a china dish was added gradually a solution of NaOH (50g, 1.25 mol) in water (30 ml). The reaction mixture sets into a hard mass with considerable evolution of heat. The ivory colored castor soap thus formed was pulverised thoroughly. An aqueous molar solution showed a pH of 10, thus demonstrating a buffer system.

Thermolysis of "castor soap". Fromation of sebacic acid, 2-octanone and 2-octanol

Neat castor soap (100g, ~ 0.074 mol) was heated with a Bunsen burner. The castor soap melts and gradually decomposes. The inside temperature never rises above 240°C. The course of the reaction can be monitored by the presence of misty vapours above the reaction mixture as long as decomposition is in progress, which usually lasts for 7 hr. The volatile products were removed by slow distillation lasting 4 hr. The distillate on fractionation gave 18.9g of fraction consisting essentially of 2-octanol and 2-octanone in the ratio 2:1. This analysis was done on the basis of isolation of crystalline 2-octanone semicarbazone, mp 121°, directly as well as after PCC oxidation. The estimated yields of 2 octanol and 2-octanone are respectively, 49% and 24%. The residue was repeatedly extracted with boiling water and cooled to give 5.0g (12%) of sebacic acid (3), mp 131° (lit. mp 133°).

Reduction of non-enolizable ketones with castor soap

General procedure: An intimate mixture of the ketone (10 mmol) and castor soap (10g; ~22 mmol hydride equivalent) was held at an inside temperature of 240° for 2 hr, cooled, digested with water, extracted with ether, washed with brine, dried ($MgSO_4$), solvents evaporated and the residue chromatographed on silica gel. The products were isolated by elution with solvents, appropriate in each case [tetraphenyl cyclopentadiene, benzene:hexane::40:60; enone 10, benzene; fluorenone, benzene:hexane::25:75; benzhydrol, benzene:EtOAc::85:15]. All products were identified by comparison with authentic samples. The details are given in Table III.

Reduction of hydrazones with castor soap

General procedure: An intimate mixture of the hydrazone (~ 20 mmol) and castor soap (20g, 44 mmol hydride equivalent) was held at an inside temperature of 240° for 4 hr, cooled, digested with water, extracted with ether, washed with brine,

dried($MgSO_4$), solvents evaporated and the residue chromatographed on silica gel Elution with hexane:benzene::90:10 gave the hydrocarbons, whose structures were confirmed by comparison with authentic samples. The details are given in Table IV.

The decomposition of camphor tosylhydrazone(11) to camphene(12) with castor soap

An intimate mixture of camphor tosylhydrazone (11)[20] (3.2g, 0.02 mol) and castor soap (20g,~ 44 mmol hydride equivalent) was held at an inside temperature of 240°, cooled, digested with water, extracted with ether, washed with brine, dried ($MgSO_4$), solvents evaporated and the residue on chromatography over silica gel and elution with hexane:benzene::80:20 gave 1.2g (80%) of camphene (12) whose ir and nmr was identical to that of an authentic sample.

Reduction of aromatic nitro compounds with castor soap

General procedure: An intimate mixture of the aromatic nitro compound (20 mmol) and castor soap (30g;~ 66 mmol hydride equivalent) was held at an inside temperature of 240° for 2 hr. The reaction mixture was then distilled and an aliquot converted to the picrate derivatives. Details are given in Table V.

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