Table I: Kaliation of Ketones at 20° [a]

Compd	Time (min) 50%[b]	100%[b]	Enolate yield, %[c]	Enolate (less:more substd)[d]
Acetone	0.5	1.5	90	
2-Heptanone	0.5	1.5	100	46:54
3-Me-2-butanone	0.5	1	101	88:12
3,3-DiMe-2-butanone	2.0	5	97	
2,4-DiMe-3 pentanone	2.5	10	100	
Isobutyrophenone	3.5	12	93	
Cyclohexanone	0.5	1.5	88	
2-Methylcyclohexanone	2.0	6	95	33:67

[a] 25.0 mmol of ketone, 28–32 mmol of KH in ~50 ml of THF. Glyme solvents are also satisfactory. No evidence of reduction was observed. [b] Per cent reaction was determined by gas evolution. [c] Determined by quenching samples containing hydrocarbon standards in water followed by glpc analysis. Ketone was absent in enolate solutions by ir. [d] By silylation at −78°. Silyl ethers isolated had spectra consistent with structures.

change in the composition is observed in 1 hr at −78°. However, if the enolate solution (0.4 *M*) is stirred at −78° for 0.75–1.0 hr with 0.08 equiv of free ketone, the enolates are reequilibrated to a mixture containing >98.5% less substituted isomer.

Alkylation and silylation may be carried out without difficulties *in situ* in the presence of excess KH.

The solutions of potassium enolates may be transformed into lithium enolates by metathesis with lithium bromide in THF; KBr precipitates immediately upon mixing. In the case of pinacolone, the cation exchange was accompanied by a shift in the enolate ir absorption from 1568 to 1604 cm^{-1}, consistent with tighter association of the lithium ion with the more electronegative end of the anion. The preparation of enolates of di- and trivalent cations is in progress.

Current preparations of enolates are often based upon lithium amides.[10,11] However, varying amounts of addition to the carbonyl group appear to occur even with the highly hindered lithium diisopropylamide. Moreover, lithium enolates are far less reactive (10^{-3}–10^{-4}) than potassium enolates,[13a] and lithium halides do not precipitate from ethereal solvents to assist metathesis reactions.

The exceptionally high reactivity of KH toward ketones provides a novel direct route to highly reactive potassium enolates. The facile formation of these intermediates provides new possibilities for investigation of enolate chemistry.

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(16) (a) Standard commercial samples of these hydrides were purchased from Alfa Products Division of Ventron Corp. (b) This sample was purchased from Ventron Corp. In contrast to usual samples of NaH, it was white rather than grey. Examination with a calibrated field microscope showed a wide range of partical sizes, with the modal size being a needle of 3-μm diameter. Potassium hydride appears as rough cubes of modal diameter 6–8 μm. Sedimentation in pentane indicated a much higher percentage of very fine particles in the NaH than in the KH. (c) Other factors possibly affecting reactivity have been discussed in reference 1, footnote 15.
(17) Infrared spectra was determined using a Perkin-Elmer Model 521 spectrometer in scale change scan mode, relative to the 1944-cm^{-1} absorption of polystyrene, in ~0.50 *M* THF solution.
(18) Reduction of norcamphor by NaH in competition with metalation has been reported by J. S. McConaghly, Jr., and J. J. Bloomfield, *J. Org. Chem.*, **33**, 3425 (1968).
(19) This highly selective monomethylation was surprising as it has been reported[3,7] that potassium enolates equilibrate much too rapidly for selective monoalkylation. Preliminary results in our laboratories suggest that the extremely high reactivity of potassium enolates compared to lithium enolates in alkylation[13a] creates difficulties in assuring that alkylation agent is present in excess.

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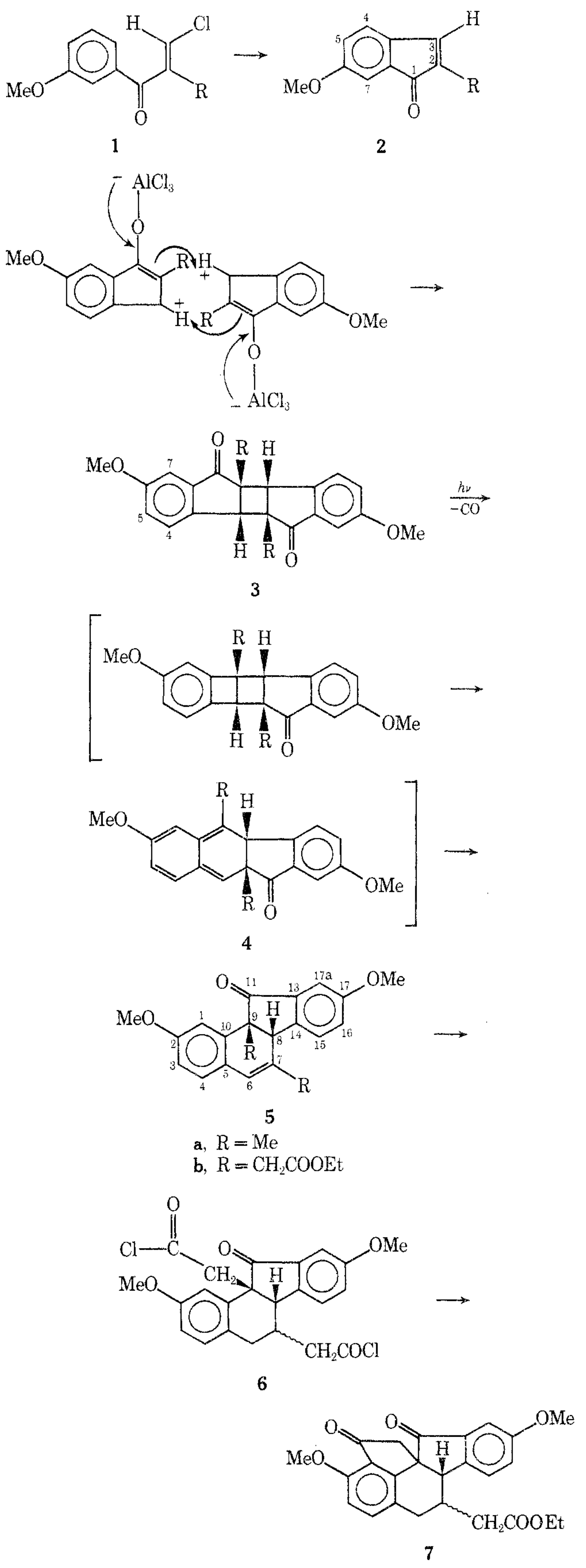
Photochemical Transformation of Truxones to C-Nor-D-homo Steroid Systems

Summary: Photodecarbonylation of truxones leads to benzobicyclohexene systems which undergo a rearrangement to products with a C-nor-D-homo steroid skeleton.

Sir: In the synthesis of 6-methoxyindenones **2** through the $AlCl_3$-catalyzed internal ketovinylation of the corresponding β-chlorovinyl ketones **1**,[1] we observed the formation of small to large amounts of truxones, which were identified as endo head-to-tail dimers **3**.[2] The ability of the 6-methoxy group to stabilize a positive charge on the C_3 is probably responsible for this easy $AlCl_3$-catalyzed dimerization, which does not occur with 2-ethyl-5-methoxyindenone, even at much higher temperatures.[3] In an attempt to obtain the indenone **2a** through a photocycloreversion from the dimer **3a**, a new product was obtained, which, according to the mass spectral analysis, should correspond to a decarbonylated dimer. A 16-hr irradiation of the endo dimer **3a** with a high pressure mercury lamp afforded 54% of the decarbonylated product and 46% indenone **2a**. This decarbonylated product was identified as **5a**, a product with a C-nor-D-homo steroid skeleton. An alternative structure **4a** was rejected as the product showed no long-wavelength absorption (400 nm) as is observed in comparable *o*-quinodimethanes.[4] The decarbonylated product did not show any Diels–Alder activity with tetracyanoethylene, as was expected for **4a**.

The nmr spectrum of the decarbonylated product shows a coupling constant of 1.5 Hz between one of the methyl groups and the vinylic proton. This is in good agreement with structure **5a**, but not with structure **4a**, where a coupling across six bonds is required. In C_6D_6 1-H undergoes a large downfield shift (0.54 ppm) which is expected for structure **5a** but not for the corresponding proton in structure **4a**. The dimer **3b** gives analogous results. According to the mass spectral data of the rearranged product **5b**, the most important fragmentation is loss of CH_3COOEt from the molecular ion (M − 88). This indicates that the 8-H and the 9-CH_2COOEt are located at



the same side of the five-membered C ring. This is also proved by the following conversions. The styrene double bond of the product **5b** has been hydrogenated and the resulting diester converted into the corresponding bis acid chloride **6**. Friedel–Crafts internal acylation afforded the product **7**. The fact that this internal acylation was possible proves the cis junction between the B and C ring in the starting steroid. In the case of a trans junction such a cyclization would not be possible, according to molecular models. The orientation of the 7-carboethoxymethyl is not clear and more experiments are needed to clarify this point.[5] The product **5** could be formed by a photochemical disrotatory ring opening of the benzobicyclohexene system, followed by a thermal 1,5-sigmatropic shift of the remaining benzoyl group. Since no product resulting from migration of the benzylic hydrogen in **4** was observed and since the migratory aptitude of an hydrogen is greater than for an acyl group in similar rearrangements,[6] this mechanism is less likely. An alternative mechanism[7] consists of a photochemical "type I" cleavage of the cyclobutyl–carbonyl bond in the benzobicyclohexene intermediate. This cleavage, followed by benzoyl migration and ring opening, could lead to compound **5**. Stereospecificity can be accounted for by the rigidity of the cyclobutyl ring.

Studies about the mechanism are under investigation together with the synthesis of mixed dimers of different methoxyindenones, with respect to the synthesis of new C-nor-D-homo steroid systems, which are interesting intermediates in the synthesis of C-nor-D-homo analogs of natural steroids[8] and of some natural steroidal alkaloids.[9]

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Supplementary Material Available. Some experimental details will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy of \$2.00 for microfiche, referring to code number JOC-74-1325.

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