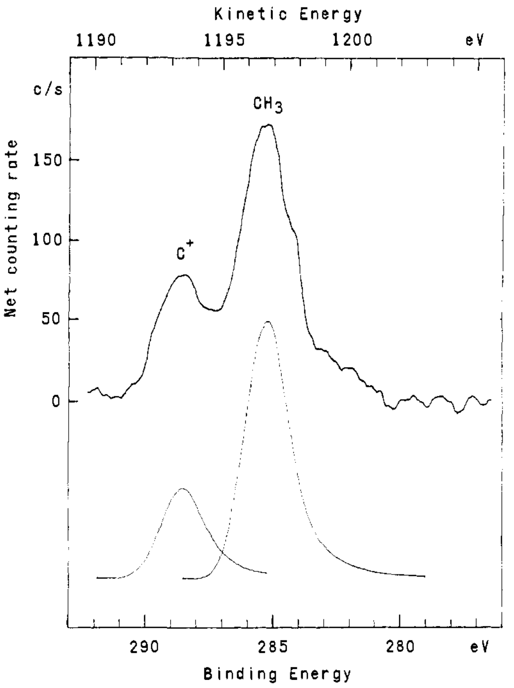

Figure 1. Carbon 1s photoelectron spectrum of *tert*-butyl cation (see text).

1, upper trace) exhibits two clearly separate peaks with E_b = 285.2 and 288.6, respectively.

The lower traces in Figure 1 represent the result given by a curve resolver[6] assuming two gaussian peaks with an integrated area ratio of 1:3. However, for a best fitting, we had to apply a slight skewing on the right wings of the curves. This suggests that the distribution is not perfectly gaussian. The background is not represented in Figure 1.

The precursor (*tert*-butyl chloride) gave a single, slightly broader line centered at 284.1 eV. No distinction of the central carbon peak was possible. It must be pointed out that these values do not represent absolute binding energies. We have used the carbon 1s line of graphite as reference (E_b = 284 eV), but no study of the effect of superacid on graphite itself and on the work function and surface potential has yet been carried out. We feel, however, that relative (internal) chemical shifts are very important in determining the electronic structure of a given cation. Indeed, our data correlate satisfactorily with *ab initio* calculations carried out by Pople and coworkers.[7] (Their absolute values given in Table I are 5–8% higher than the experimental ones.)

The experimental carbon 1s binding energy difference (3.4 eV) between the carbenium ion center and the remaining three carbon atoms is about 1 eV smaller than that predicted by *ab initio* calculation (4.45 eV).

Trityl and tropylium hexafluoroantimonates were measured in solid state. A few milligrams of fine powder (mixed with graphite) was uniformly spread on an adhesive tape and wrapped around a cylindrical sample holder. The trityl cation peak (E_b = 284.7 eV) does not exhibit any significant broadening (in comparison with triphenylmethyl chloride). Thus it is obvious that an extensive positive charge delocalization occurs in this ion. The tropylium cation also gives a single 1s line at practically the same position as the trityl cation.

We are presently carrying out further investigations in order to find a suitable internal standard reference. We are also extending the photoelectron spectroscopic studies to other organic ions. Detailed aspects of this work will be reported in a full paper.

Acknowledgment. We are grateful to Professor John A. Pople for communicating results of his calculations ahead of publication.

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[6] Du Pont Model 310 curve resolver.

[7] J. A. Pople, L. Radom, and P. v. R. Schleyer, personal communication.

The Total Synthesis of DL-Alnusenone

Sir:

An earlier report[1] from this laboratory presented the advantages to a program directed toward the total synthesis of a variety of pentacyclic triterpenes of a scheme that had as its initial goal the synthesis of members of the friedelin group. The specific synthetic plan designed for this task has as its central feature the construction of the pentacyclic diether **9**, which after sequential modification of the terminal aromatic rings would provide access to the triterpenoid ketone alnusenone (**13**).[2] The realization of this initial goal in preliminary form is the subject of this report and sets the stage for the broader investigation of the transformations of pentacyclic derivatives most readily available through synthesis.

The results of our previous investigation[1] suggested that the synthetically most difficult structural feature of the pentacyclic diether **9** was not so much its pentacyclic character but the trans-oriented C-6a and C-14a angular methyl groups. Subsequent work[3] has therefore focused on overcoming this problem early in the synthetic program. One such approach entails the establishment of the desired trans orientation of the potential C-6a and C-14a angular methyl groups in an appropriate tricyclic intermediate from which the desired B/C trans-fused pentacyclic diether **9** can be formed through closure of ring B by an acid-catalyzed process.

In order to realize the logistic advantages of a convergent synthesis[4] we chose to investigate the sequence outlined in Chart I. Our plan called for the formation of the requisite tricyclic olefin mixture **7** through the agency of conjugate cyanide addition to the readily available[1] α,β-unsaturated ketone **3** (bp 193–195° (0.01 mm)). In fact, utilization of the elegant pro-

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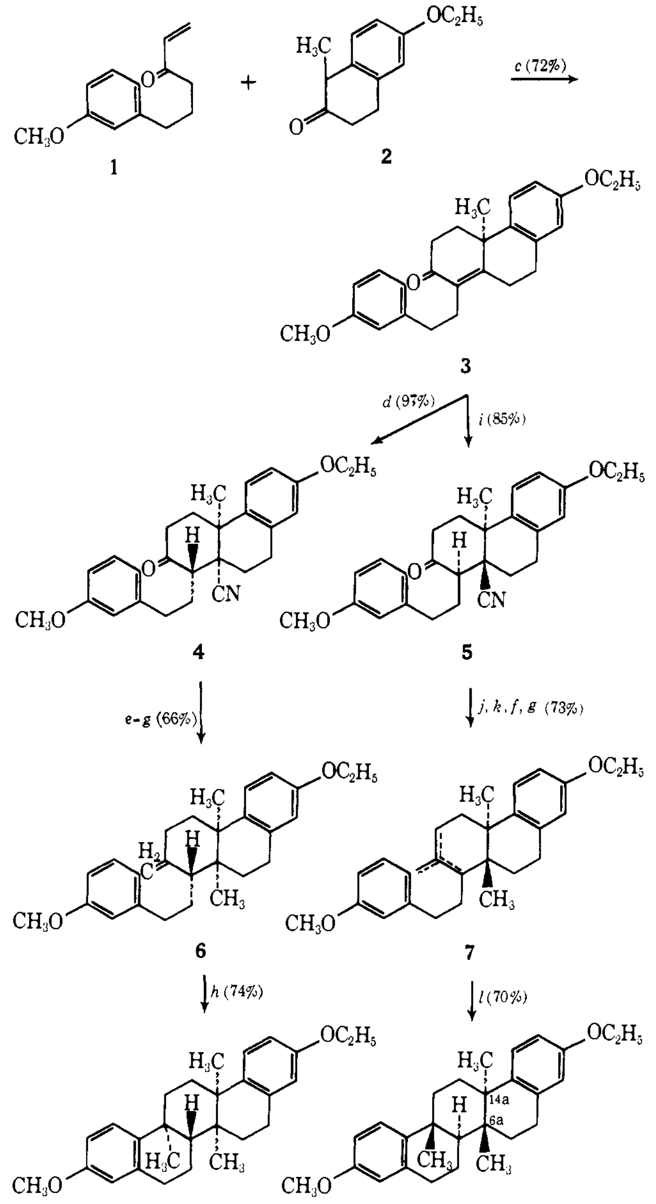
(1) R. E. Ireland, D. A. Evans, D. Glover, G. M. Rubottom, and H. Young, *J. Org. Chem.*, 34, 3717 (1969).

(2) J. M. Beaton, F. S. Spring, and R. Stevenson, *J. Chem. Soc.*, 2616 (1955).

(3) R. E. Ireland, M. I. Dawson, J. Bordner, and R. E. Dickerson, *J. Amer. Chem. Soc.*, **92**, 2568 (1970); R. E. Ireland, D. R. Marshall, and J. W. Tilley, *ibid.*, **92**, 4754 (1970.)

(4) L. Velluz, J. Rallo, and G. Nominé, *Angew. Chem., Int. Ed. Engl.*, 4, 181 (1965); see also R. E. Ireland, "Organic Synthesis," Prentice-Hall, Englewood Cliffs, N. J., 1969, pp 28–30.

Chart I. The Synthesis of *trans,anti,cis*- and *trans,anti,trans*-Pentacyclic Diethers 8 and 9[a,b]



[a] All intermediates were characterized by ir and nmr spectroscopy, and the spectral data are fully consistent with the structures assigned. All new substances isolated gave satisfactory combustion analyses. [b] Except for alnusenone (13), the pentacyclic compounds shown are described by the picene nomenclature and numbering (A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd ed, American Chemical Society, Washington, D. C., 1960, No. 6384) and each racemate is arbitrarily represented by that enantiomer that has the 12b methyl group in the β configuration. [c] KOH, CH_3OH. [d] $(C_2H_5)_2AlCN$, C_6H_6. [e] $(C_6H_5)_3P{=}CH_2$. [f] $(i\text{-}Bu)_2AlH$, C_6H_6. [g] $N_2H_4 \cdot 2HCl$, $N_2H_4 \cdot H_2O$, KOH, TEG, Δ. [h] PPA, 60°, 1 hr. [i] $(C_2H_5)_3Al$, HCN, THF. [j] CH_3MgI. [k] $SOCl_2$, pyr, 0°. [l] *p*-TsOH, $C_6H_5CH_3$, Δ.

cedures for such conjugate cyanide additions developed by Nagata and coworkers[5] resulted in the efficient formation of either stereoisomeric cyano ketone **4** or **5** at will. Thus, under aprotic conditions (Et_2AlCN–C_6H_6)[5b] the thermodynamically more stable *cis*-cyano ketone **4** (mp 142–143°) was formed almost exclusively, while in a protic medium (Et_3Al–HCN–THF)[5c] the trans isomer **5** (mp 132–133°) was virtually the sole product of kinetically controlled cyanide attack. These stereochemical assignments were initially made on the basis of the spectral (ir, nmr) characteristics[6] of the two cyano ketones, and firm confirmation of the correctness of the evaluation of these data was obtained through single-crystal X-ray structure analysis[7] of the *trans,anti,cis*-pentacyclic diether **8** (mp 153–154°) prepared from the *cis*-cyano ketone **4** in the manner shown (Chart I).

Interestingly, the *trans*-cyano ketone **5** failed to react with methylenetriphenylphosphorane under a variety of conditions and was either recovered unchanged or suffered dehydrocyanation. However, the addition of methylmagnesium iodide was successful and dehydration with thionyl chloride–pyridine afforded a mixture of the cyano olefins which on reduction[8] of the cyano group provided a satisfactory overall yield of the mixture of tricyclic olefins **7** (mp 95–100°). Cyclization of this mixture in toluene with *p*-toluenesulfonic acid catalysis then afforded the desired *trans,anti,trans*-pentacyclic diether **9** (mp 152–153°) in 31% overall yield from the tetralone **2**.

The next stage in the synthetic scheme requires the selective reduction of the aromatic E ring. In order to prevent[9] the reduction of the A ring during this process the pentacyclic diether **9** was first converted to the phenolic ether **10** (mp 184–185°) through selective demethylation with lithium diphenylphosphide[10] (Chart II). Reduction of this phenolic ether **10** was complicated by the low solubility of its lithium salt in ammonia–cosolvent systems but was accomplished with a 20-fold molar excess of lithium in dilute 1:1 ammonia–tetrahydrofuran solution in the presence of ethanol. After the excess lithium was destroyed and the ammonia removed, methyl iodide was added to remethylate the C-10 phenoxide, and then treatment of the crude reduction product with aqueous mineral acid afforded a moderate yield of the methoxy enone **11** (mp 206–208°). As expected[11] the conjugate addition of lithium dimethylcuprate to this enone **11** failed completely and an alternate method for the introduction of the C-4a,β angular methyl group was developed (Chart II). The intermediate cyclopropyl ketone required for this process was formed by Simmons–Smith cyclopropylation[12] of the corresponding allylic alcohol and also proved to be an excellent substrate

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(5) (a) W. Nagata and M. Yoshioka, *Proc. Int. Congr. Horm. Steroids, 2nd, Milan*, 327 (1966); (b) W. Nagata and M. Yoshioka, *Tetrahedron Lett.*, 1913 (1966); (c) W. Nagata, M. Yoshioka, and S. Hirai, *ibid.*, 461 (1962).

(6) P. N. Rao and J. E. Burdett, Jr., *J. Org. Chem.*, **34**, 1090 (1969); W. Nagata, M. Yoshioka, M. Narisada, and H. Watanabe, *Tetrahedron Lett.*, 3133 (1964).

(7) The complete details of this crucial analysis, expertly executed by Dr. Jon Bordner and Professor Richard E. Dickerson (Caltech), will be included in the forthcoming definitive report of this work.

(8) A modified procedure for the Wolff–Kishner reduction of hindered ketones originally reported by W. Nagata and H. Itazaki [*Chem. Ind. (London)*, 1194 (1964)] was found particularly useful for the reduction of the intermediate imine formed after diisobutylaluminum hydride reduction of the cyano group.

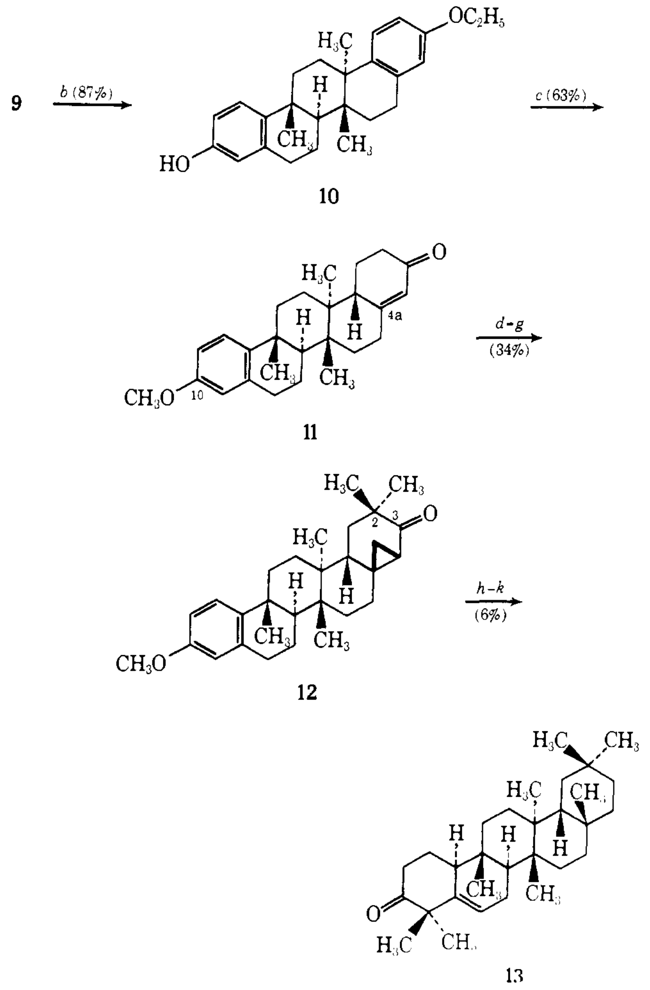
(9) For another example of such selectivity during a Birch reduction, see J. Fried and N. A. Abraham, *Tetrahedron Lett.*, 3505 (1965); J. Fried, N. A. Abraham, and T. S. Santhanakrishnan, *J. Amer. Chem. Soc.*, **89**, 1044 (1967).

(10) F. G. Mann and M. J. Pragnell, *Chem. Ind. (London)*, 1386 (1964).

(11) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, **31**, 1016 (1966).

(12) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **80**, 5323 (1958); **81**, 4256 (1959).

Chart II. The Conversion of the *trans,anti,trans*-Pentacyclic Diether 9 to DL-Alnusenone (13)[a]



[a] See Chart I, footnotes *a* and *b*. [b] $LiP(C_6H_5)_2$ (1 equiv), THF. [c] Li, NH_3, C_2H_5OH, THF; CH_3I; H_3O^+. [d] $(i\text{-}Bu)_2AlH$, C_6H_6. [e] CH_2I_2, Zn(Cu), ether-THF. [f] CrO_3-Py_2, CH_2Cl_2. [g] KO-*tert*-Bu, THF, CH_3I. [h] Li, NH_3, THF, NH_4Cl. [i] N_2H_4-2HCl, $N_2H_4 \cdot H_2O$, KOH, TEG, Δ. [j] Li, NH_3, C_2H_5OH, H_3O^+. [k] KO-*tert*-Bu, *tert*-BuOH, C_6H_6, CH_3I.

for the introduction of C-2 *gem*-dimethyl grouping through direct base-catalyzed methylation. In model systems as well as the case at hand, high yields of the bismethylated product were realized.

Of the remaining transformations of the cyclopropyl ketone **12** (mp 177–178°) that led to *dl*-alnusenone (**13**), only the Wolff-Kishner reduction of the highly hindered C-3 ketone formed after lithium-ammonia cleavage[13] of the cyclopropane system afforded a poor yield. The 16% yield of reduced material obtained during this preliminary investigation will undoubtedly be improved by further experimentation. Despite this low yield sufficient material was obtained to allow modification of the aromatic A ring according to the procedures used earlier in the synthesis of *dl*-rimuene,[14] and the high yields realized during these latter transformations provided a sample of the racemic triterpene (**13**): mp 208–208.5°; nmr (220 MHz) ($CDCl_3$) δ 0.82 (3 H), 0.96 (3 H), 1.00 (3 H), 1.03 (3 H), 1.10 (3 H), 1.17 (3 H), 1.23 (3 H), 1.24 (3 H) (s, quaternary CH_3), and 5.71 (m, 1, C-6 H); ir ($CHCl_3$) 3020 (vinyl H), 1700 (>C=O), and 1655 cm^{-1} (>C=C<); glc (0.125 in. × 6 ft 10% W-98 on Chromosorb W at 300° with 50 ml/min He flow) retention time 6.5 min; tlc (silica gel, 10% ether–petroleum ether (30–60°)) R_f = 0.41. *Anal.* Found: C, 84.83; H, 11.40. This material, obtained after 17 steps, was identical with an authentic sample of (+)-alnusenone, mp 245–247°, kindly provided by Professor Robert Stevenson as determined by comparison of the glc and tlc retention times and solution ir and nmr (220 MHz) spectra. Further work is in progress to refine and develop the later stages of this successful reaction scheme and to investigate its utility for the synthesis of other pentacyclic triterpenoid systems.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

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tert-Butyl Peroxyformate. A Convenient Source of Hydrogen Atoms in Solution. Reactions of the Hydrogen Atom. V[1,2]

Sir:

Recently we reported detailed kinetic studies of the reactions of the hydrogen atom in solution.[2] This species is important both because of theoretical considerations[3,4] and also because it has been implicated in radiation chemistry and biology.[5–7] In our previous studies[2] the hydrogen atoms were generated by the solution photolysis of thiols (eq 1), and relative values

$$RSH \xrightarrow{h\nu} RS\cdot + H\cdot \qquad (1)$$

of k_H were reported for a series of organic hydrogen donors QH.

$$H\cdot + QH \xrightarrow{k_H} H_2 + Q\cdot \qquad (2)$$

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