Table I. Rate Constants for Quenching of Triplet Butyrophenone[a] by Various Olefins

Olefin	$k_q\tau$[b]	k_q, $10^7\ M^{-1}\ sec^{-1}$ [c]
$CH_2{=}CH{-}CH{=}CH{-}CH_3$	580	500
$(CH_3)_2C{=}C(CH_3)_2$	52.5	46 ± 3
$(CH_3)_2C{=}CH{-}CH_3$	15.0	14 ± 1.5
$CH_2{=}C(CH_3)CH_2CH_3$	3.2	2.8 ± 0.2
cis-$CH_3CH{=}CHCH_2CH_3$	4.0	3.0 ± 1.0
trans-$CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3$	1.25	1.1 ± 0.2
trans-*t*-BuCH=CH*t*-Bu	1.9	2.4
$CH_2{=}CHCH_2CH_2CH_3$	0.90	0.8
Cyclopentene	6.1	5.2 ± 0.1
Norbornene	3.4	3.7 ± 0.1
Cyclohexene	4.2	4.2 ± 1.5
1,4-Cyclohexadiene	11.6	14.6
cis-ClCH=CH—Cl	18	16 ± 0.1
$Cl_2C{=}CHCl$	82	72 ± 5
$Cl_2C{=}CCl_2$	165	145 ± 1

[a] 0.10 *M* butyrophenone in benzene at 25°, irradiated at 3130 Å. [b] Generally the average of two or more runs. [c] Errors represent mean deviation from average, none shown for single runs.

Table II. Quenching Rates of Select Olefins toward Various Energy Triplets

	Quencher, k_q, $10^7\ M^{-1}\ sec^{-1}$			
Quenchee (E_T)	RCH=CHR	$Me_2C{=}CHMe$	$Me_2C{=}CMe_2$	ClCH=CHCl
Benzene (84)[a]	~500	~500	~500	~500
Acetone (78–80)[b,c]	~1	~2	~5	
PhCOPr (74.5)[d]	1–5	14	46	16
$PhCOCH_3$ (73.5)[b]	1–2			
PhCOPh (68.5)	8[e]	20[f]	170[f]	1.3[g]

[a] See ref 8. [b] Reference 3. [c] Reference 7. [d] This work. [e] Reference 2. [f] N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, **89**, 5465 (1967). [g] Reference 4.

of an intermediate besides the biradical. Such π complexing to electrophilic species is a characteristic reaction of olefins and is thought to occur in the photocycloaddition reactions of α,β-unsaturated cyclic ketones.[18]

Two further observations deserve attention. The chloroethylenes are much better quenchers of butyrophenone than are the analogous alkylethylenes. Such behavior is consistent only with energy transfer being the major quenching process, since both C–T complexing and radical addition would be slowed by increasing chloro substitution.[19]

The behavior of the cyclic olefins is especially interesting in that they are all significantly better quenchers than are the *cis*-1,2-dialkylethylenes. Furthermore, ketones with triplet excitation energies >73 kcal sensitize dimerization of the strained cycloalkenes.[1] Our study of the dependence of butyrophenone-sensitized cyclopentene and norbornene dimer quantum yields on olefin concentration suggests that as much as one-half of the total quenching may involve energy transfer. Unless the dimerization somehow does not involve olefin triplets, we must conclude that triplet energy transfer to the strained cycloalkenes is considerably faster than to the unstrained alkenes. This behavior is reasonable only if the π,π^* triplets undergo rehybridization to an sp^3-like configuration at the olefinic carbons.[20]

All the alkenes and cycloalkenes seem to give small amounts of oxetanes. With none of the olefins we studied does product formation (loss of butyrophenone) account for more than 20% of the total quenching, except for cyclohexene, where photoreduction[1] products are evident. If a charge-transfer complex is indeed formed, the efficiency with which it collapses to a biradical and the partitioning of the biradical are obviously subtle functions of olefin structure. Therefore it is not possible to correlate oxetane yields with the mechanism of quenching.

Finally, the quenching efficiency of 1,4-cyclohexadiene is not out of line with that displayed by many other olefins, so that we question the necessity of invoking a new mechanism such as vibrational quenching.[5]

Acknowledgments. We thank the Research Corporation for support of the initial stages of this work, the National Science Foundation for overall support, and Mr. John R. Barber for performing very useful preliminary experiments.

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(18) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

(19) Caldwell has reached the same conclusion from a study of isotope effects.[4] Moreover, dichloroethylene quenches triplet benzophenone ($E_T \sim 69$ kcal) only 1/20th as fast as it quenches triplet butyrophenone.

(20) A. D. Walsh, *J. Chem. Soc.*, 2325 (1953); D. R. Arnold and V. Y. Abraitys, *Mol. Photochem.*, 2, 27 (1970).

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Received March 5, 1970

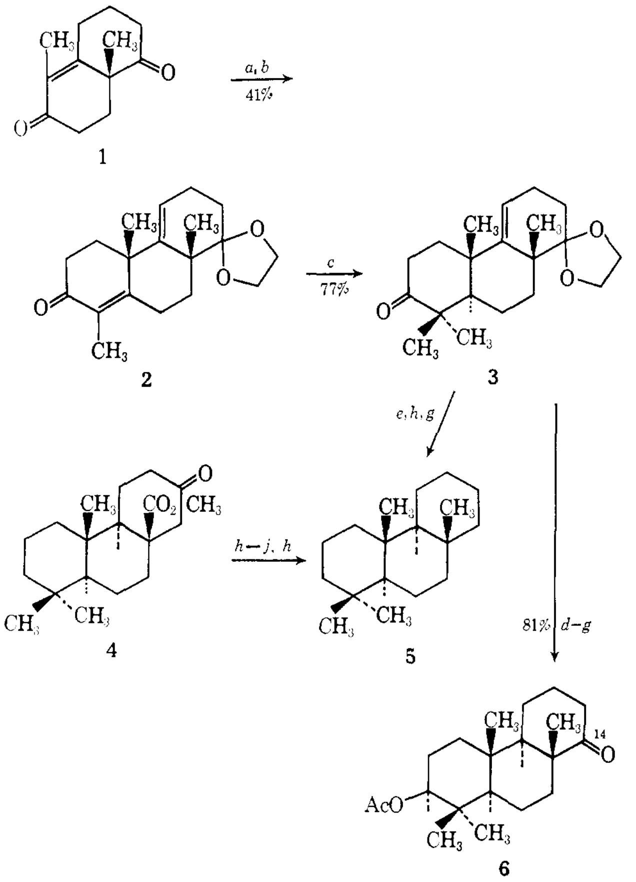
The Total Synthesis of an Unsymmetrical Pentacyclic Triterpene. DL-Germanicol

Sir:

For some time a portion of the effort of these laboratories has been directed toward the development of reaction patterns suitable for the total synthesis of the logistically demanding, unsymmetrically substituted pentacyclic triterpenes. The overall concept of this joint program entailed first the construction of a tricyclic intermediate which embodies the characteristics common to the ABC rings of many triterpenoids. The addition of the D and E rings to such an intermediate may then be planned so as to provide synthetic routes to a wide variety of naturally occurring pentacyclic triterpenoid systems. The initial pentacyclic objective of that portion of the work undertaken at the Michigan and Caltech laboratories was germanicol (**20**),[1] and we report here the pertinent status of the program and the successful culmination of the phase that has led to this triterpene.

Our work began with the synthesis of the tricyclic keto acetate **6** (mp 161–162.5°) which was made available in 22% overall yield from 2-methyl-1,3-cyclohexanedione by the procedures outlined in Chart I. Verification of the stereochemical assignments made at this state was found in the conversion of the keto ketal **3** (mp 98.5–99°) and the keto ester **4** to the same hydrocarbon **5** (oil, evap dist 80° (0.1 mm)). The stereochemistry of the keto ester **4** is firmly established by virtue of the central role it plays in the degradation and synthesis of the diterpene phyllocladene.[3] The identity of the two samples of the hydrocarbon **5** was established by solution ir spectroscopy and confirmed the trans–anti–trans configuration assigned to the keto acetate **6**.

Chart I. Synthesis and Structure Proof of Tricyclic Intermediate **6**[2]



[a] $(CH_2OH)_2$, H^+. [b] $C_2H_5COCH{=}CH_2$, $NaOCH_3$, CH_3OH. [c] Li, NH_3, *tert*-BuOH, CH_3I. [d] $LiAl(O\text{-}tert\text{-}Bu)_3H$. [e] H_3O^+. [f] Ac_2O, pyr. [g] H_2, Pd–C, HOAc. [h] N_2H_4, OH^-, DEG. [i] $SOCl_2$, C_6H_6. [j] H_2, Pd–$BaSO_4$.

Further modification of this material requires that provision be made for the efficient, stereoselective introduction of two unlike carbon residues at C-14 and functionality for D ring formation at C-13. The two approaches that were investigated (Chart II) differed in the stage at which oxidation of the C-13 methylene was undertaken. In one approach, this oxidative step was accomplished first, and the keto acetate **6** was converted to the diosphenol methyl ether **7** [mp 197–198.5°, λ^{EtOH} 261 mμ (ϵ 6100)] and then to the aldehyde **9** (R = H) (mp 152–154°). While these transformations were quite efficient, methylation of this highly hindered aldehyde was difficult and proceeded only in 50% yield. However, the sole product of this methylation process was later shown (see below) to be the desired aldehyde **9** ($R = CH_3$) (mp 149–152°) by its conversion, in five steps, to the lactone acetate **11** (mp 249–250.5°). This latter material was available in good yield from the degradation[4] of the tetracyclic triterpene euphol (**13**) and solution infrared and nmr spectroscopy proved the identity of the samples from the two sources. Fortuitously, the synthetic lactone acetate **11** from euphol (**13**) crystallizes as a racemic mixture which was resolvable by mechanical separation of the crystals obtained by slow crystallization from acetonitrile. Mixture melting point determination (mmp 287.5–288°) and the identity of the optical rotatory dispersion curve of the (+) enantiomer (mp 289.5–290°; $[\alpha]^{25}$D +35°, *c* 1.02, CH_2Cl_2) of the synthetic lactone acetate **11** with that of the naturally derived lactone acetate (mp 287.5–288.5°; $[\alpha]^{25}$D +35°, *c* 1.00, CH_2Cl_2) provided confirmation of a link between the two series and proof of the configuration at C-14 of the totally synthetic material. The identity of these samples also afforded a convenient relay, and lactone acetate **11** from the euphol (**13**) degradation was used for the preparation of an authentic sample of the diketone **14** (mp 187.5–189.5°; $[\alpha]^{25}$D +13°, *c* 1.427, $HCCl_3$) for comparison with racemic material from the other scheme.

A preparatively more efficient modification of the keto acetate **6** involved the initial introduction of a carbon residue at C-14, followed by oxidation of the C-13 methylene group. This process (Chart II) led through the readily available olefinic ketal **8** (mp 168–169°) to the methylene ketone **10** (mp 160–163°). The ease with which such systems undergo conjugate addition reactions opened several avenues for the attachment of the requisite C-14 substituents. For the case at hand conjugate addition of *m*-methoxybenzylmagnesium chloride followed by methylation of the derived enol acetate **12** (mp 109–111°) proved to be an excellent means for the synthesis of the racemic diketone **14**

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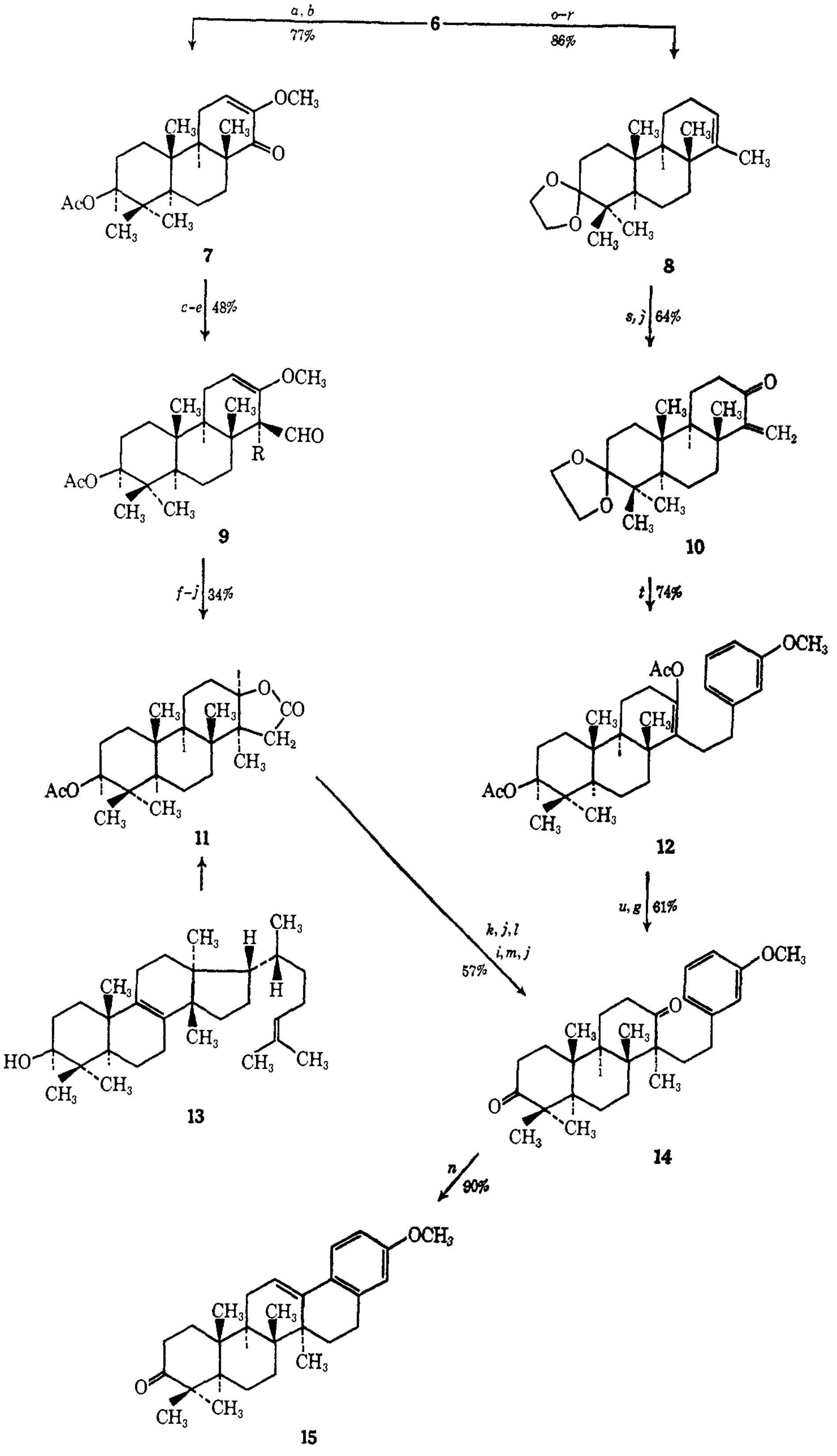
(1) For the isolation and structure proof see J. Simonsen and W. C. J. Ross, "The Terpenes," Vol. IV, Cambridge University Press, New York, N. Y., 1957, pp 247–252.

(2) All intermediates were characterized by ir and nmr spectroscopy which are fully consistent with the structures shown. All new substances gave satisfactory combustion analyses.

(3) (a) P. K. Grant and R. Hodges, *Tetrahedron*, **8**, 261 (1960); (b) R. F. Church, R. E. Ireland, and J. A. Marshall, *J. Org. Chem.*, **31**, 2526 (1966); (c) R. B. Turner, K. H. Gänshirt, P. E. Shaw, and J. D. Tauber, *J. Amer. Chem. Soc.*, **88**, 1776 (1966).

(4) The procedures used in this work were a modification and extension of those reported by D. Arigoni, R. Viterlo, M. Dunnenberger, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **37**, 2306 (1954), and D. Arigoni, O. Jeger, and L. Ruzicka, *ibid.*, **38**, 222 (1955). It is noteworthy that the euphol need not be separated from the companion substance euphorbol, since the latter also leads to the lactone **11**.

Chart II. Conversion of Tricyclic Keto Acetate 6 to Pentacyclic Ketone 15 and Correlation with Euphol (13)[2]



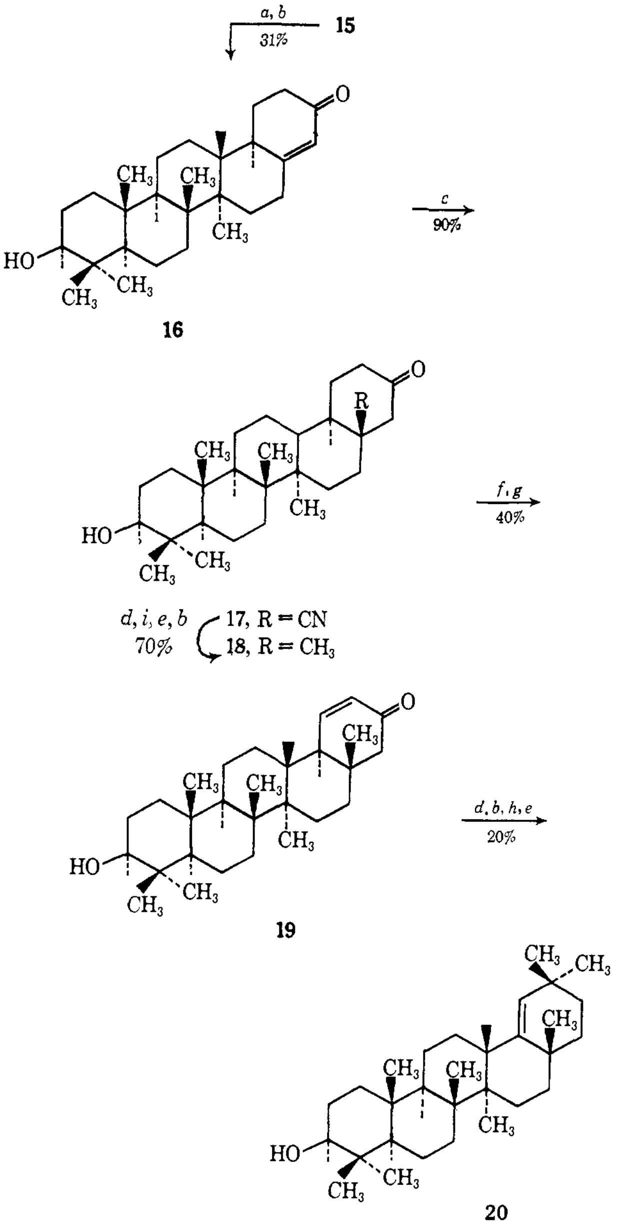
[a] Br$_2$, HOAc. [b] OH$^-$, (CH$_3$)$_2$SO$_4$, Ac$_2$O, pyr. [c] NaCH$_2$SO$^+$(CH$_3$)$_2$, Ac$_2$O, pyr. [d] BF$_3 \cdot$Et$_2$O. [e] NaH, DMSO, CH$_3$I. [f] (C$_6$H$_5$)$_3$P=CH$_2$. [g] H$_3$O$^+$. [h] LiAl(O-*tert*-Bu)$_3$H. [i] R$_2$BH, H$_2$O$_2$, OH$^-$. [j] CrO$_3 \cdot$2Py. [k] OH$^-$. [l] (CH$_2$OH)$_2$, H$^+$. [m] *m*-CH$_3$OC$_6$H$_4$MgBr, H$_2$, Pd–C. H$_3$O$^+$. [n] PPA. [o] CH$_3$Li, DME. [p] 8 *N* H$_2$CrO$_4$, acetone. [q] SOCl$_2$, pyr. [r] *p*-TsOH. C$_6$H$_6$, (CH$_2$OH)$_2$. [s] O$_2$, *hν*, sensitizer, pyr, LiAlH$_4$. [t] *m*-CH$_3$OC$_6$H$_4$CH$_2$MgCl, Ac$_2$O. [u] CH$_3$Li, DME, CH$_3$I.

(mp 124–124.5°) in 25% overall yield from the keto acetate **6**.

That the racemic diketone **14** prepared by this procedure had the desired structure and stereochemistry was confirmed through solution ir and nmr (60 and 220 MHz) spectral comparison with optically active material obtained from euphol (**13**) (see above). Since the racemic diketone **14** was so readily available, we preferred to carry out further synthetic operations with this material rather than that derived from euphol (**13**). Cyclization of the racemic diketone **14** by treatment with polyphosphoric acid for 30 min at 25° produced the important pentacyclic intermediate **15** (mp 147.5–150°) in high yield.

The final conversions that led to *dl*-germanicol (**20**) are outlined in Chart III. It is to be emphasized that, at the present stage of development, the yields have not been optimized. In separate experiments it was possible to show by nmr spectroscopy that potassium–ammonia–ammonium chloride reduction of the 12,13 double bond in model systems similar to the pentacyclic ketone **15** leads to the production of significant quantities of C/D cis-fused (C-13 α hydrogen) material[5] in addition to the predominant formation of the desired C/D trans-fused (β-C-13 hydrogen) substance. While it was not possible to isolate the corresponding C/D cis-fused material from the lithium–ammonia–alcohol reduction used for the formation of the hydroxy enone **16** (mp 263.5–268.5°), the low yield of this step may be a function of its formation.

Chart III. Conversion of Pentacyclic Ketone **15** to *dl*-Germanicol(**20**)^a



[a] Li, NH$_3$, alcohol. [b] H$_3$O$^-$. [c] AlEt$_3$, HCN, THF. [d] (CH$_2$OH)$_2$, H$^+$. [e] N$_2$H$_4$, OH$^-$, TEG. [f] Br$_2$, HOAc. [g] CaCO$_3$, DMA. [h] KO-*tert*-Bu, *tert*-BuOH, CH$_3$I. [i] (*i*-Bu)$_2$AlH, C$_6$H$_6$.

Introduction of the final angular methyl group at C-17, accomplished through reduction of the corresponding C-17 cyano ketone **17** (mp 316–318.5°), afforded the hydroxy ketone **18** (mp 300–303.5°) in good overall yield. The stereochemical assignment at this last asymmetric center rests on the extensive precedents provided by the work of Nagata and coworkers[6] on this sequence as well as spectral (ir, nmr) data[7] that are in agreement with those of similar systems.

Of the remaining steps in the synthesis, it is worth noting that direct methylation of the conjugated enone **19** (mp 206–209.5°) was ineffectual, and it was necessary first to deconjugate the double bond prior to methylation. The sample of totally synthetic *dl*-germanicol (**20**) had the following properties: mp 220–223°; nmr (220 MHz) (CDCl$_3$) δ 0.74 (3 H), 0.79 (3 H), 0.89 (3 H), 0.95 (3 H), 0.98 (6 H), 1.03 (3 H), 1.09 (3 H) (s, quaternary CH$_3$), 3.22 (d of d, 1, J = 10 Hz, J' = 4 Hz, C-3 H) and 4.85 (s, 1, C-19 H); ir (CHCl$_3$) 3600 cm^{-1} (C-3 OH); vpc (0.125 in. × 6 ft 4% SE-30 on Diatoport S at 300°) ret time 2.2 min; tlc (silica gel, 3.3% CH$_3$OH–HCCl$_3$), R_f = 0.65. *Anal.* Found: C, 84.35; H, 11.71. This material, obtained after 31 steps, was identical with an authentic sample of the natural triterpene kindly provided by Professor C. Djerassi as shown by comparison of the vpc and tlc retention times, and solution infrared and nmr (60 and 220 MHz) spectra. The attainment of the initial goal of this synthetic program attests to the viability of the approach and opens the way for modification and improvement of the reaction scheme.

Acknowledgment. That portion of this work carried out at Michigan and Caltech was supported by grants from the National Science Foundation and the Hoffmann-La Roche Foundation, while that at Stanford was sponsored by the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society. The authors gratefully acknowledge this support.

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[5] The C/D cis-fused ring E aromatic isomers in this series are readily recognized from their nmr spectra, in which the signal due to the β-C-8 methyl group is found at about 23 rather than 60 Hz.

[6] W. Nagata and M. Yoshioka, *Proc. Int. Congr. Horm. Steroids, 2nd, 1966*, 327 (1967).

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

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Received June 11, 1970