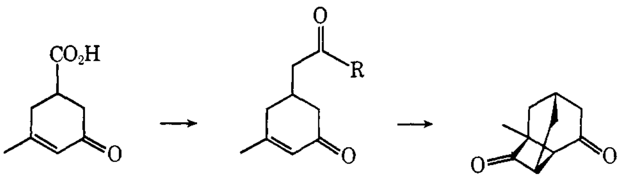
An additional system with a different relative location of the reacting sites was synthesized. Keto acid **14** was prepared by an Arndt-Eistert reaction of keto acid **13**.[15] Irradiation of diazo ketone **16** in cyclohexane or benzene enabled isolation of diketone **17**[11a] from the reaction mixture in a yield of 24%: mp 74°; ir 1782, 1710 cm^{-1}; nmr δ 3.35 (m, 1 H), 2.60 (m, 1 H), 1.20 ppm (s, 3 H); M$^+$ = 164.



13

14, R = -OH
15, R = -Cl
16, R = -CHN$_2$

17

Photochemical additions of double bonds to α,β-unsaturated ketones have been studied intensively and numerous cases of intramolecular additions are known.[16] The structures of such products have been determined, but it is not always clear what factors govern the orientation of addition. In the photochemical cycloaddition of allenes to cycloalkenones,[17] the direction of the addition was such that oxidation of the exocyclic double bond led to a 1,3-diketone.

Thus, we have presented three examples of intramolecular photochemical addition of ketenes to double bonds conjugated to ketones. It was found that the direction of addition in the cases studied in this work was such that the products contained the carbonyl groups in a 1,4 relationship, as opposed to the addition of allenes. It was shown that without excitation of the enone system no cycloaddition occurred.

(15) D. D. Phillips and A. W. Johnson, *J. Org. Chem.*, **21**, 587 (1956).

(16) (a) G. Büchi and I. M. Goldman, *J. Amer. Chem. Soc.*, **79**, 4741 (1957); (b) C. H. Heathcock and R. A. Badger, *Chem. Commun.*, 1510 (1968); (c) W. F. Erman and T. W. Gibson, *Tetrahedron*, **25**, 2493 (1969).

(17) (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) P. E. Eaton, *Tetrahedron Lett.*, 3695 (1964); (c) K. Wiesner, S. Uyeo, A. Philipp, and Z. Valenta, *ibid.*, 6279 (1968).

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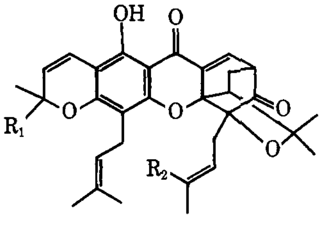
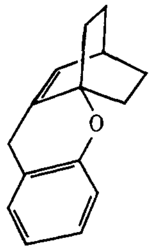
Two Syntheses of the 2,4a-Ethano-2,3,4,4a-tetrahydroxanthene System

Sir:

The naturally occurring compounds morellin (**1**)[1] and gambogic acid (**2**)[2] and their relatives have a nucleus consisting of the 2,4a-ethano-2,3,4,4a-tetrahydroxanthene system (**3**). We describe two novel synthetic routes to this system.[3]

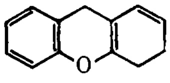


1, R$_1$ = Me; R$_2$ = CHO
2, R$_1$ = CH$_2$CH$_2$CH═CMe$_2$; R$_2$ = CO$_2$H



3

The first involves the Diels–Alder reaction of dienophiles with 3,4-dihydroxanthene (**4**). The diene **4**,[4] mp 32–34° [$\lambda_{\max}^{\mathrm{CCl_4}}$ 5.92 (m) μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 290 (6400), 298 (sh, 6000), 314 (sh, 3700) nm; $\delta^{\mathrm{CDCl_3}}$ 2.29 (d, J = 2 Hz, 4 H), 3.29 (s, 2 H), 5.56 (m, 1 H), 5.68 (d, J = 9 Hz, 1 H), 6.96 (m, 4 H)], was prepared from the dihydroxanthenone **5**[5] by treatment of its tosylhydrazone **6**, mp 219–220°, with methyllithium. Reaction of **4** with dimethyl acetylenedicarboxylate gave the adduct **7**, mp 92–96° [$\lambda_{\max}^{\mathrm{CCl_4}}$ 5.70, 5.78, 5.97 (w), 6.09 (w) μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 269 (2100), 278 (1700), 305 (650) nm; $\delta^{\mathrm{CDCl_3}}$ 1.70 (m, 4 H), 3.48 (br s, 2 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 4.17 (d of t, J = 6, 3 Hz, 1 H), 6.11 (d of t, J = 6, 2 Hz, 1 H), 7.04 (m, 4 H)]. Reaction of **4** with propiolonitrile gave the adduct **8**, mp 75–78° [$\lambda_{\max}^{\mathrm{CCl_4}}$ 4.54 (m) μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 270 (1600), 276 (1400) nm; $\delta^{\mathrm{CDCl_3}}$ 1.62 (m, 4 H), 3.40 (d of d, J = 17, 1.5 Hz, 1 H), 3.51 (d of d, J = 17, 2 Hz, 1 H), 3.71 (m, 1 H), 5.95 (d of t, J = 6, 2 Hz, 1 H), 7.14 (m, 5 H)]. The structures of these adducts follow from their pmr spectra and the conversion of **8** at 163° to 4-cyanoxanthene (**9**), mp 91–93° [$\lambda_{\max}^{\mathrm{CCl_4}}$ 4.49 (w) μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 252 (7000), 279 (2100), 307 (4200) nm; $\delta^{\mathrm{CDCl_3}}$ 4.04 (s, 2 H), 7.29 (m, 7 H)], further characterized as the corresponding acid **10**, mp 185–186° (lit.[6] mp 183°) [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 3.04 (m), 5.76, 5.86 (sh) μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 248 (8200), 279 (2400), 303 (2800) nm], and methyl ester **11**, mp 48–49° [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.82 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 248 (8200), 278 (2300), 305 (3200) nm; $\delta^{\mathrm{CDCl_3}}$ 3.94 (s, 3 H), 3.99 (s, 2 H), 7.11 (m, 6 H), 7.72 (d of d, J = 7, 2 Hz, 1 H)].



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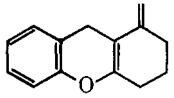
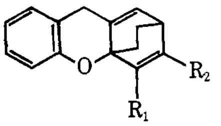
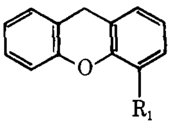


5, X = O
6, X = NNHTos



7, R$_1$ = R$_2$ = CO$_2$Me
8, R$_1$ = CN; R$_2$ = H



9, R$_1$ = CN
10, R$_1$ = CO$_2$H
11, R$_1$ = CO$_2$Me

(1) G. Kartha, G. N. Ramachandran, H. B. Bhat, P. M. Nair, V. K. V. Raghavan, and N. Venkataraman, *Tetrahedron Lett.*, 459 (1963); F. M. Nair and K. Venkataraman, *Indian J. Chem.*, **2**, 402 (1964); H. B. Bhat, P. M. Nair, and K. Venkataraman, *ibid.*, **2**, 405 (1964); C. G. Karanjgaonkar, P. M. Nair, and K. Venkataraman, *Tetrahedron Lett.*, 687 (1966).

(2) P. Yates, S. S. Karmarkar, D. Rosenthal, G. H. Stout, and V. F. Stout, *ibid.*, 1623 (1963); W. D. Ollis, M. V. J. Ramsay, I. O. Sutherland, and S. Mongkolsuk, *Tetrahedron*, **21**, 1453 (1965); S. A. Ahmad, W. Rigby, and R. B. Taylor, *J. Chem. Soc. C*, 772 (1966); M. Amorosa and G. Giovanninetti, *Ann. Chim. (Rome)*, **56**, 232 (1966); G. Cardillo and L. Merlini, *Tetrahedron Lett.*, 2529 (1967).

(3) Very recently another synthesis has been reported by A. J. Quillinan and F. Scheinmann, *Chem. Commun.*, 966 (1971).

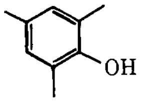
(4) Acceptable elemental analyses have been obtained for all compounds characterized by melting point; parent peaks for these compounds have been observed in their low-resolution mass spectra.

(5) Prepared by condensation of 1,3-cyclohexanedione with *o*-hydroxybenzyl alcohol in HMPA; *cf.* P. Yates, D. J. Bichan, and J. E. McCloskey, *Chem. Commun.*, in press.

(6) S. Akagi and T. Iwashige, *J. Pharm. Soc. Jap.*, **74**, 610 (1954).

The second route developed to system **3** involves the intramolecular Diels–Alder reaction of a 6-acryloxy-2,4-cyclohexadienone formed by a novel variant of the Wessely oxidation. The feasibility of this pathway was investigated by treatment of mesitol (**12**) in acrylic acid with lead tetraacetate at room temperature. This gave the dienone **13**, which was not isolated, but was converted at 70° to **14**, mp 111–112° [$\lambda_{\max}^{\mathrm{CCl_4}}$ 5.58, 5.74 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ 312 (ϵ 180) nm; $\delta^{\mathrm{CDCl_3}}$ 1.26 (s, 3 H), 1.44 (s, 3 H), 1.93 (d, J = 2 Hz, superimposed on m, 5 H), 2.84 (d of d of d, J = 9, 5, 2 Hz, 1 H), 3.30 (d of d, J = 5, 2 Hz, 1 H), 5.79 (br s, 1 H)]. The structure of the latter was established by its spectra and its conversion on treatment with aqueous base followed by periodic acid to the lactol **15** [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 3–4, 5.71, 5.86 μ; $\delta^{\mathrm{C_5H_5N}}$ 1.50 (s, 3 H), 1.82 (s, 3 H), 2.23 (br s, 3 H), 2.45 (m, 1 H), 3.15 (m, 2 H), 3.53 (m, 1 H), 6.07 (br s, 1 H)]; this was converted by lead tetraacetate to **16**, mp 56–57.5° [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.64 μ; $\delta^{\mathrm{CDCl_3}}$ 1.40 (s, 3 H), 1.42 (s, 3 H), 1.90 (d, J = 2 Hz, 3 H), 2.0–2.6 (m, 3 H), 3.19 (d of d, J = 4, 2 Hz, 1 H), 6.12 (br s, 1 H)], which on treatment with palladium/charcoal in refluxing 2-methoxyethanol gave 3,5-dimethylbenzoic acid.

The xanthene **17**[7] on treatment in acrylic acid with lead tetraacetate at room temperature gave the dienone **18**, which was not isolated but was converted at 80° to **19**, mp 116–118° [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.58, 5.72 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 271 (1410), 275 (1380), 310 (200) nm; $\delta^{\mathrm{CDCl_3}}$ 1.39 (s, 3 H), 1.84 (d of d of d, J = 13, 11, 2 Hz, 1 H), 2.26 (d of d of d, J = 13, 3.5, 1.5 Hz, 1 H), 2.70 (d of d, J = 11, 1.5 Hz, 1 H), 3.42 (d of d of d, J = 7, 3.5, 2 Hz, 1 H), 3.59 (d, J = 2 Hz, 2 H), 6.28 (d of t, J = 7, 2 Hz, 1 H), 7.14 (m, 4 H)].



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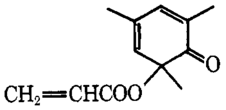

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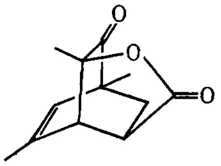

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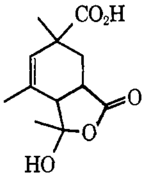

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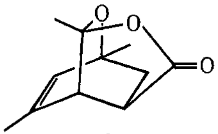

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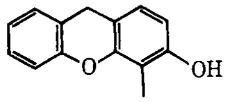

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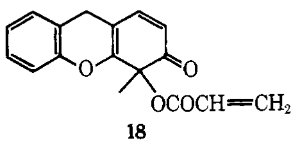

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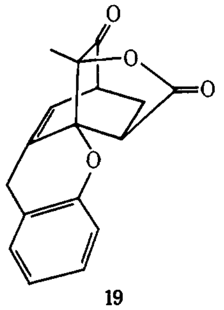

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(7) Prepared by reduction of 3-hydroxy-4-methylxanthone[8] with lithium aluminum hydride; *cf.* A. Mustafa and O. H. Hishmat, *J. Org. Chem.*, **22**, 1644 (1957).

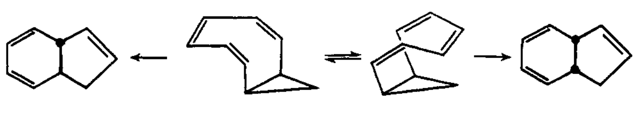
(8) Y. S. Agasimundin and S. Rajagopal, *Monatsh. Chem.*, **97**, 423 (1966).

Epimerization at the 9 Position in Substituted Bicyclo[6.1.0]nona-2,4,6-trienes[1]

Sir:

Compounds containing the bicyclo[6.1.0] skeleton display a wide variety of rearrangements and have posed particularly vexing problems of mechanism.[2] The unsubstituted molecule[3–5] and 9-monosubstituted compounds[6–8] rearrange mainly to *cis*-dihydroindenes. 9,9-Dialkyl-substituted compounds, by contrast, give predominantly *trans*-dihydroindenes.[9–11] When the 9 position is substituted with a cyano group,[12,13] a spirofluorene[14] or a spirocyclopentadiene,[15] bicyclo[4.2.1]nonatrienes are produced.

It has been suggested[9,10] that the *cis*-dihydroindenes are formed from the coiled arrangement (**1**) and the *trans*-dihydroindenes from the extended form (**2**).



2 **1**

This explains the reluctance of the 9,9-disubstituted compounds to give the cis product as the coiled form should be severely destabilized by endo-9 substitution.[16]

A long-standing problem has been the behavior of *endo*-9-methylbicyclo[6.1.0]nonatetraene (**3a**). Although one might reasonably expect this compound to mimic the 9,9-dimethyl substance, which also possesses an endo methyl group, it does not. Like its epimer **3b**, the products of rearrangement are mainly *cis*-dihydroindenes.[8] The recent report[17] that the products of thermal rearrangement of **3a** are not identical with

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(1) Support of this work by the National Science Foundation through Grants GP-12759 and 30797X is warmly acknowledged. We also express our appreciation for helpful comments by Professor Paul von R. Schleyer and Dr. F.-G. Klärner.

(2) For a review, see: S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

(3) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

(4) W. Grimme, Halibitätionsschrift, Köln, 1968.

(5) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(6) K. F. Bangert and V. Boekelheide, *J. Amer. Chem. Soc.*, **86**, 905 (1964).

(7) G. J. Fonken and W. Moran, *Chem. Ind. (London)*, 1841 (1963).

(8) P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1560 (1969).

(9) S. W. Staley and T. J. Henry, *ibid.*, **91**, 1239 (1969).

(10) S. W. Staley and T. J. Henry, *ibid.*, **91**, 7787 (1969).

(11) W. Grimme, private communication, 1970.

(12) A. G. Anastassiou, R. P. Cellura, and E. Ciganek, *Tetrahedron Lett.*, 5267 (1970).

(13) F.-G. Klärner, *ibid.*, 3611 (1971).

(14) M. E. Hendrick, unpublished observation.

(15) D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969).

(16) Conrotatory opening of the extended form to a cyclononatetraene containing a trans double bond followed by disrotatory closure allows formation of *trans*-dihydroindene. No mechanism has yet been proposed which accounts for the conversion of the coiled form to *cis*-dihydroindene without the intrusion of an orbital symmetry forbidden step or the intervention of diradicals.

(17) A. G. Anastassiou and R. C. Griffith, *Chem. Commun.*, 1301 (1971).