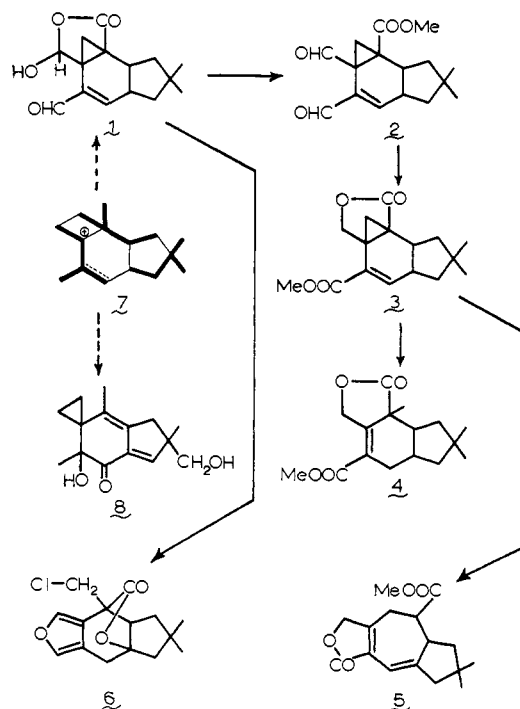1 H; singlet, τ 0.17, 1 H). Treatment with aqueous base induces an internal Cannizzaro reaction leading, after methylation, to 3 (m.p. 127–128°; [α]D +80°; λmax 233 mμ (ε 6300); νmax 1767, 1709, and 1634

cm.⁻¹; signals at τ 8.98 (3 H, singlet) 8.95 (3 H, singlet), 6.20 (3 H, singlet), 5.52 (2 H, AB pattern, J_{AB} = 10 c.p.s., $δ_B − δ_A$ = 20.7 c.p.s.), and 3.35 (1 H, doublet, $J \sim 2$ c.p.s.).

In these substances signals for two methyl groups attached to quaternary carbon can be discerned. Hydrogenation of 3 to the dihydro compound (4, m.p. 110–111°; [α]D +96°; λmax 231 mμ (ε 10,100); νmax 1773, 1709, and 1675 cm.⁻¹) gives, by 1,4-addition to the vinylcyclopropane system, a substance in which a signal for a third methyl group (τ 8.71) can be observed. The latter substance, unlike 3, shows no signal for vinylic proton absorption but has a band at 4.83 (2 H, broad) for allylic protons on carbon bearing oxygen.

This sequence provides direct evidence for the presence of the cyclopropane ring for which spectroscopic evidence was also available. The position of this cyclopropane ring within the concatenation of carbonyl functions was shown by the conversion of 3 under more strongly basic conditions to 5 (m.p. 142–143°; [α]D +216°; λmax 274 mμ (ε 7500); νmax 1754, 1736, and 1686 cm.⁻¹; signals at τ 9.03 (3 H, singlet), 8.90 (3 H, singlet), 6.27 (3 H, singlet), 5.30 (2 H, singlet), and 3.86 (1 H, singlet). This transformation represents a vinylogous extension of the base-catalyzed opening of homocaronic acid.[3]

Treatment of marasmic acid with refluxing hydrochloric acid in acetic acid resulted in cleavage of the cyclopropane ring and cyclization to the lactonic furan 6 (m.p. 93–94°; [α]D −13°; λmax 215 mμ (ε 5300); νmax 1776 cm.⁻¹). The furan nature of 6 was shown by the formation of a Diels–Alder adduct with acetylenedicarboxylic ester. In addition, every proton with its expected coupling could be identified and clearly

(3) G. Widmark, Arkiv Kemi, 11, 195 (1957).

discerned in the n.m.r. spectrum[4] [signals at τ 8.92 (3 H, singlet), 8.80 (3 H, singlet), 8.04 (2 H, AB pattern, J_{AB} = 15 c.p.s., $δ_B − δ_A$ = 26 c.p.s.), 7.8–8.7 (2 H, AB of ABX), 7.08 (2 H, AB, J_{AB} = 17 c.p.s., $δ_B − δ_A$ = 23.5 c.p.s.), 7.3 (1 H, X of ABX, doublet of doublets), 6.12 (2 H, AB, J_{AB} = 12 c.p.s., $δ_B − δ_A$ = 21.9 c.p.s.), and 2.76 and 2.66 (1 H each, narrow with fine splitting)]. The lack of coupling between the pair of methylene protons in the cyclopentane ring required that they be separated by the geminal methyl groups. Confirmation of this and of the entire carbon skeleton was obtained by the classical method of dehydrogenation.

Reduction of marasmic acid with sodium borohydride and treatment with palladized charcoal at 300° gave two aromatic hydrocarbons. Spectroscopic data required that these be methylated indans, and the more substituted was identified as 2,2,4,5,6-pentamethyl-indan by direct synthesis.[5] This substance contains all the carbon atoms of marasmic acid except that present in the carboxyl function. Structure 1 follows unequivocally.

The structure of marasmic acid as here presented represents a new mode of cyclization of a farnesyl precursor. The most likely biogenetic route appears to be that through an ion such as 7; in principle this may be obtained by a direct cyclization. It is pertinent that the formation of marasmic acid and of illudin-S (8)[6] represents two alternative migrations in the same cyclobutyl cation (7).

(4) Using deuterium chloride the resultant furan had incorporated three deuterium atoms. These were the two fuanic protons and one of the adjacent methylene protons. On irradiation of the deuterium, kindly performed by Dr. J. B. Stothers, a one-proton singlet was obtained instead of the AB pattern in the undeuterated material.

(5) The less substituted was identified as 2,2,4,5-tetramethylindan by synthesis of 2,2,4,6-tetramethylindan, the only other possible isomer.

(6) T. C. McMorris and M. Anchel, J. Am. Chem. Soc., 85, 831 (1963); M. Tuda, Y. Yamada, N. S. Bhacca, K. Nakanishi, and M. Ohashi, Chem. Pharm. Bull. (Tokyo), 7, 853 (1964); K. Nakanishi, M. Tada, and Y. Yamada, ibid., 7, 856 (1964); T. C. McMorris and M. Anchel, J. Am. Chem. Soc., 87, 1594 (1965).

J. J. Dugan, P. de Mayo, M. Nisbet
Department of Chemistry, University of Western Ontario
London, Ontario, Canada

M. Anchel
New York Botanical Garden
New York 58, New York

Cyclopentadienone Ketals

Sir:

We wish to present an exceptionally convenient synthesis of the ketals of cyclopentadienone and to report the use of these active dienes in the preparation of 7-substituted norbornenes. Further, we wish to draw attention to the extraordinary influence of the ketal group on the reactivity of these dienes.

Cyclopentadienone would seem in theory to be the most suitable reagent for norbornenone syntheses. Unfortunately this dienone has but fleeting existence; spontaneous dimerization occurs even at very low temperatures. In 1962 DePuy[1] and Vogel[2] recognized independently that the ketals of cyclopentadienone would possess the synthetic utility of the parent ketone

(1) C. H. DePuy, B. W. Ponder, and J. D. Fitzpatrick, Angew. Chem., 74, 489 (1962); J. Org. Chem., 29, 3508 (1964).
(2) E. Vogel and E.-G. Wyes, Angew. Chem., 74, 489 (1962).

but should be of more temperate reactivity. Both succeeded in the indirect preparation of cyclopentadienone ethylene ketal but, quite contrary to expectation, this compound too dimerized with remarkable facility and could not be employed in the usual crossed Diels–Alder reactions. To explore this further we have prepared the methyl, ethyl, trimethylene, and ethylene ketals of cyclopentadienone by a new route and have examined their synthetic utility and relative reactivity.

In our synthesis of these various compounds the appropriate ketal of cyclopentanone is dissolved in the alcohol from which it is derived and treated just below room temperature with 2 molar equiv. of pyridinium bromide perbromide. The reaction leads to consistently good yields (75–95%) of the corresponding ketals of 2,5-dibromocyclopentanone as colorless or yellow oils. Double dehydrobromination can be accomplished by addition of any of the bromoketals to a twofold excess of potassium *t*-butoxide in dimethyl sulfoxide at 18–20°. The reaction mixture is processed immediately by quenching in ice–water and extracting the unsaturated ketal into cold pentane.

If the pentane solution of the cyclopentadienone ketal so produced is let stand overnight an excellent yield (70–95%) of the Diels–Alder dimer is obtained. The structure of each ketal dimer has been demonstrated unambiguously by hydrolytic conversion to *endo*-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione, the well-known dimer of cyclopentadienone.[3] Indeed, this method provides by far the best approach to this interesting compound.

The methyl, ethyl, and trimethylene ketals of cyclopentadienone, but not the ethylene ketal, can be intercepted easily with 1 molar equiv. of maleic anhydride, tetracyanoethylene, or *p*-benzoquinone. Even lesser dienophiles such as acrolein can be employed successfully if used in large excess. The addition of 1 molar equiv. of maleic anhydride to the pentane extracts from dehydrobromination of 2,5-dibromocyclopentanone ethyl ketal leads after suitable work-up to a 70% yield of the Diels–Alder adduct I, m.p. 84–85.5°. In equal fashion the adducts to tetracyanoethylene (m.p. 185.5–187°) and to *p*-benzoquinone (II, m.p. 79.8–81.5°) can be prepared in 76 and 60% yield, respectively. The reaction of cyclopentadienone ethyl ketal with excess acrolein gives a mixture of adducts (III, b.p. 75–76° (0.8 mm.)). Such adducts may be converted to the corresponding 7-norbornenones by removing the ketal masking group. Adduct I is transformed to the bridge ketone IV (m.p. 152–152.5°) by treatment with aluminum chloride in dichloromethane. Similarly aqueous sulfuric acid converts the benzoquinone adduct II into the unusual triketone V (m.p. 118–119.5°). Thus, these reactions provide an excellent approach to 7-substituted norbornenes well suited to facile synthetic elaboration.

By a simple modification we have been able to expand the scope of this method to include the preparation of norbornenone derivatives substituted at the bridgehead position. The bromination of cyclopentanone methyl ketal with 3 molar equiv. of pyridinium bromide perbromide and subsequent dehydrobromination of the product gives the bromodiene

VI. This ketal too is an active Diels–Alder diene; for example, reaction with *p*-benzoquinone leads to the adduct VII, m.p. 112–113.5°. With a reliable method for the production of such compounds now in hand, the path (*cf.* the cubane synthesis[4]) is open to the synthesis of a wide variety of provocative cage systems.
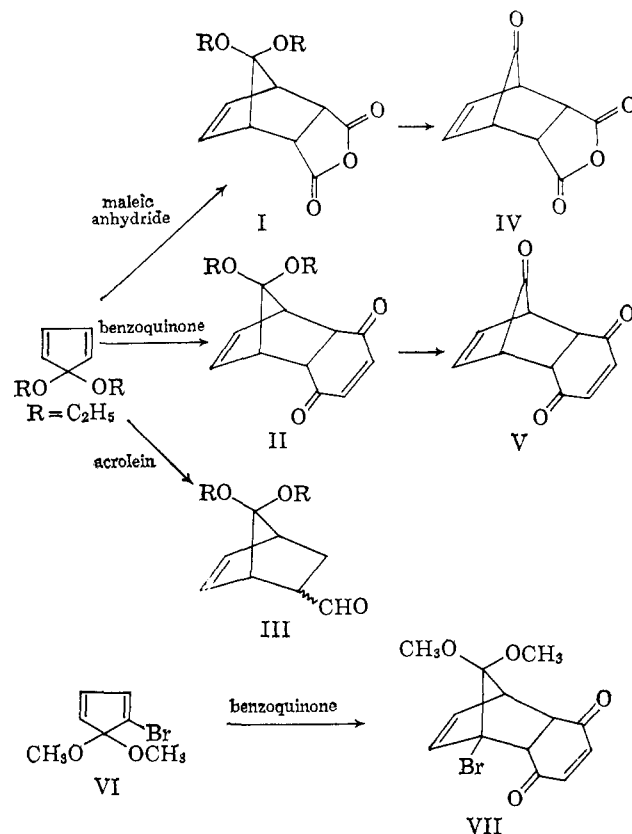
We have measured spectrophotometrically the relative second-order rate constants for dimerization of the methyl, ethyl, trimethylene, and ethylene ketals of cyclopentadienone. These are, respectively, 1.7, 1.0, 14, and 1070 at 25°. For comparison, the ethyl ketal of cyclopentadienone dimerizes about 465 times more rapidly than cyclopentadiene; the ethylene ketal dimerizes nearly *500,000 times faster than cyclopentadiene.* A rationalization for these differences can be constructed from a liberal combination of electronic and steric effects; however, a sound explanation must await the report of further experiments.

Although the reactivities and the ultraviolet spectra of these dienes cannot yet be bound together by any certain ties, note is made here of the significant bathochromic shifts which accompany the introduction of alkoxyl groups onto the saturated carbon of cyclopentadiene. The ultraviolet absorption maximum in pentane for cyclopentadiene and for the methyl, ethyl, trimethylene, and ethylene ketals of cyclopentadienone appears at 239, 270, 270, 272, and 280 mμ, respectively. It is particularly striking that the ethylene ketal, the most reactive member of the series, exhibits the largest shift to the red.[5]

(3) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).

(4) P. E. Eaton and T. W. Cole, Jr., *ibid.*, **86**, 3157 (1964).

(5) *Cf.* W.-H. Chang, *Chem. Ind.* (London), 709 (1964).

National Aeronautics and Space Administration for a predoctoral graduate fellowship.

Philip E. Eaton,[6] Richard A. Hudson

*Department of Chemistry, The University of Chicago*
Chicago, Illinois
Received October 16, 1964

Mechanism of the Diels–Alder Reaction.
The Question of the "Internal" Pathway for the Thermal endo–exo Isomerizations of the 5-Norbornene-2,3-dicarboxylic Anhydrides[1]

Sir:

Much information bearing on the mechanism of the Diels–Alder reaction has been obtained from studies of isomerizations of various adducts of cyclopentadiene.[2-11] One of the most interesting and important of these isomerizations is the conversion of the endo-cyclopentadiene–maleic anhydride adduct [5-norbornene-2,3-endo-dicarboxylic anhydride (N)[12]] to the corresponding exo isomer (X) at 190°.[13] Berson and co-workers[2,3] have made a detailed study of this process
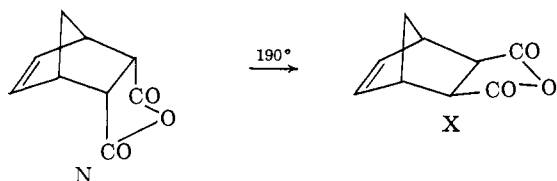
and have reported that in decalin it takes place *both* by an "external" pathway (a retrogression of the endo adduct N to the addends which then recombine to give the exo isomer X) and an "internal" pathway (a direct mechanism not involving dissociation into kinetically free fragments).

In connection with a projected study of the stereochemistry of these reactions using the endo adduct asymmetrically labeled with ^{14}C, we have re-examined the case for the occurrence of the "internal" pathway.

The following observations prompted our studies. First, under the conditions reported for the N to X conversion [0.102 M N and maleic anhydride (M) in boiling decalin, 190°], not all of the maleic anhydride is in solution. In addition, a fairly considerable amount of M sublimes out of the reaction mixture within a few minutes. Obviously, in these circumstances there is no longer an equimolar quantity of M present. As a consequence the results become prejudiced toward the internal pathway.[14]

(1) Supported in part by the National Science Foundation.
(2) J. A. Berson and R. D. Reynolds, *J. Am. Chem. Soc.*, **77**, 4434 (1955).
(3) J. A. Berson, R. D. Reynolds, and W. M. Jones, *Ibid.*, **78**, 6049 (1956).
(4) J. A. Berson, A. Remanick, and W. A. Mueller, *ibid.*, **82**, 5501 (1960).
(5) J. A. Berson and W. A. Mueller, *Ibid.*, **83**, 4940 (1961).
(6) J. A. Berson and A. Remanick, *ibid.*, **83**, 4947 (1961).
(7) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).
(8) P. Yates and P. Eaton, *Tetrahedron Letters*, No. 11, 5 (1960).
(9) P. Yates and P. Eaton, *Tetrahedron*, **12**, 13 (1961).
(10) R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, No. 22, 29 (1960).
(11) J. E. Baldwin and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 115 (1963).
(12) For convenience, the same symbols will be used in this paper as by Berson and co-workers.[2,3]
(13) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).
(14) The evidence previously obtained for the internal pathway by

Table I. Exchange between Radioactive N and X with Inactive M Compared to the Rate of Formation of X

Starting material[a]	Reaction time, min.	Activity recovd., %[b]	X formed, %[c]
N	2	81.06	3.3
N	4	71.11	5.5
N	6	63.26	7.5
N	8	59.55	10.3
N	10	57.58	11.55[d]
N	10	. . .	13.3 ± 0.15[e]
N	12	. . .	16.1
X	10	97.9	. . .
X[f]	10	98.1	. . .

[a] Starting concentrations: 0.267 M radioactive N (436.10 μc./mole) or X (440.84 μc./mole) and 0.267 M inactive M. [b] Per cent of original activity in recovered starting material. [c] Determined by n.m.r. integration in $CHCl_3$ from the mixture of N and X by comparison of the ratio of a peak belonging to X only with one common to the sum of N and X. [d] This value is regarded as being somewhat low. [e] Average of three separate runs. [f] Starting concentration: 0.0267 M radioactive X (440.84 μc./mole) and 0.267 M inactive M.

To get around these difficulties we have studied the N to X isomerization in *t*-pentylbenzene which gives homogeneous solutions and permits use of 0.267 M N (labeled with ^{14}C in both carbonyl carbons) and 0.267 M nonradioactive M at the boiling point (189–190°).

We have obtained quite conclusive evidence that there is in fact no internal mechanism for the thermal isomerization of the endo adduct N to the exo isomer X in *t*-pentylbenzene. The rearrangement appears to occur only by dissociation–recombination in exactly the same way as the endo–exo isomerization of the cyclopentadiene–acrylic ester[6] and 9-phenylanthracene–maleic anhydride adducts.[5]

Exchange of radioactive N with inactive M was found to occur very rapidly in comparison to the exchange of X with M (Table I).

Clearly, X is only present in small concentrations in the early stages of the exchange between N and M. Therefore it was necessary to determine the activity of X by the isotope-dilution technique.

The activities theoretically to be expected of X arising from N exclusively by an internal mechanism and by an external mechanism were calculated on the basis of the following assumptions: During any small increment of time, the X formed by the internal mechanism has the same activity as the average activity of N during that time, and the X formed by the external mechanism has the same activity as the average activity of M during that time. The data of Table I were plotted to show the decrease in activity of N with time (β_t vs. time) and the fraction of N converted to X with time (% X_t vs. time). The plots were then subdivided into arbitrarily small time increments (30 sec.). Values for the average activities of N and for the fraction of the total amount of X formed during each of the time increments were determined by graphical interpolation from the plots.

If β_0 is the original activity of N, β_1 the average activity of N during time increment 1, β_2 during time

Baldwin and Roberts,[11] based on the N to X interconversion in presence of tetracyanoethylene as a scavenger for cyclopentadiene, has been wholly vitiated by the unanticipated discovery that maleic anhydride reacts with cyclopentadiene at a rate comparable to that of tetracyanoethylene above 150° in decalin (unpublished results of U. Scheidegger) as well as in *t*-pentylbenzene.