Table I. Conversion of Substituted Acetophenones into Methyl Phenylacetates

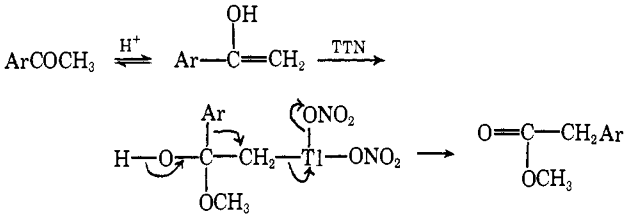
$ArCOCH_3 \longrightarrow ArCH_2COOCH_3$

Compd	Ar =	Reaction time, hr	Yield, %^{a}
1	C_6H_5	5	84
2	$4\text{-}FC_6H_4$	17	44
3	$4\text{-}CH_3C_6H_4$	4	86
4	$2\text{-}CH_3OC_6H_4$	12	62
5	$3,4\text{-}(CH_3O)_2C_6H_3$	1	88
6	$3\text{-}NO_2\text{-}4\text{-}CH_3OC_6H_3$	15	61
7	$4\text{-}HOC_6H_4$	2	64^b
8	$4\text{-}C_6H_5CONHC_6H_4$	1^c	66
9	$2\text{-}C_{10}H_7$	2	94

^{a} Calculated on pure redistilled or recrystallized material. ^{b} Refers to 4-hydroxyphenylacetic acid, obtained by hydrolysis of the crude ester with 2 *N* sodium hydroxide. ^{c} Reaction carried out at 50°.

We believe that the mechanism of this transformation is best represented as shown in Scheme I. Acid-catalyzed enolization followed by oxythallation leads to an unstable alkylthallium dinitrate. Decomposition of this intermediate proceeds *via* migration of the aryl substituent, resulting in direct formation of the methyl arylacetate and simultaneous reduction of thallium(III) to thallium(I). The essential feature of this mechanism, *viz.* 1,2-aryl migration, was readily substantiated by the simple expedient of employing acetophenone ^{14}CO as substrate. The labeled methyl phenylacetate isolated after treatment with TTN in methanol was converted into benzylamine and carbon dioxide by standard Curtius degradation of the corresponding hydrazide. All of the ^{14}C label was located in the carbon dioxide.

Scheme I



From an examination of a wide range of substituted acetophenones we have been able to define the limitations of the present conversion as follows. (i) The reaction is unsuccessful when applied to compounds containing amino substituents due to preferential complexation of the amino group with the thallium electrophile. The corresponding amides, however (*cf.* **8**, Table I), react normally. Surprisingly, *p*-hydroxyacetophenone gave a good yield of *p*-hydroxyphenylacetic acid, although some concomitant oxidation to red polymeric material also occurred. (ii) Acetophenones in which the aromatic ring is highly deactivated by electron-withdrawing substituents undergo enolization, oxythallation, and aryl migration only very slowly, and with these compounds low yields of methyl arylacetates are obtained. Within these limitations, however, the present procedure constitutes the method of choice for the conversion of acetophenones into arylacetic acids.[5,6]

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(5) The reaction is probably not applicable to acetophenones carrying unsaturated substituents since competitive oxythallation of the olefin would be anticipated.[4]

(6) Preliminary experiments have established that the above rearrangement is general for alkyl aryl ketones, and, in contrast to the Willgerodt–Kindler reaction,[2] may be used for the synthesis of α-alkyl-substituted arylacetates. This extension of the present reaction was not further pursued, however, since a much superior one-step synthesis of these latter compounds has been developed which involves treatment of alkyl arylacetylenes with TTN in methanol.[7]

(7) A. McKillop, O. H. Oldenziel, B. P. Swann, E. C. Taylor, and R. L. Robey, submitted for publication.

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Competitive Bond Rotation and Bond Scission Processes in Semistabilized 1,4 Diradicals. The Thermal Fragmentation of [4.4.2]Propella-2,4-dienes

Sir:

By the mere expediency of incorporating a cyclobutane ring into a structure endowed with reduced conformational flexibility, thermal fragmentation of the strained ring will be forced to proceed nonconcertedly *via* transient 1,4 diradicals.[1] Recent extended Hückel studies of such reactive intermediates have led to the conclusion that they are twixtylic in nature, *i.e.*, they are unstable with respect to olefin pairs and consequently do not represent true energy minima.[2] The rather surprising implications of this analysis have not been put to sound experimental test, chiefly because cyclobutane derivatives bearing sufficient stereochemical labeling and rigidity have not been available. Also, in the great majority of cyclobutanes which have been pyrolyzed to date,[3] the structural features have been such that bond rotation, ring closure, and bond scission are competitive.[4] We now describe the stereochemical consequences attending the pyrolysis of several [4.4.2]-propella-2,4-dienes.[5] These tricyclic molecules are ideally suited for the present purpose because: (a) they are incapable of extensive twisting; (b) the anticipated reduction in activation energies associated with initial bond homolysis (due to the developing cyclohexadienyl radical) should result in the need for lower pyrolysis temperatures; and (c) the driving force underlying the incipient aromatic character in the tetralin fragment was expected to appreciably enhance k_{scis} relative to k_{rot}. As a result, the average lifetimes of the derived twixtyls should be greatly minimized.

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(1) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 65 ff.

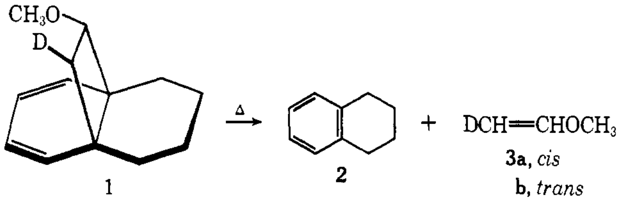
(2) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(3) (a) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966); (b) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (c) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969); (d) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); (e) A. T. Cocks and H. M. Frey, *J. Chem. Soc. A*, 1671 (1969); (f) L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970).

(4) (a) L. M. Stephenson and J. I. Brauman, *ibid.*, **93**, 1988 (1971); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(5) The synthesis of all starting materials described in this communication will be published elsewhere.

Under conditions where **1** was slowly introduced in the gas phase into a heated quartz tube (28 cm × 16 mm, 760 Torr) packed with quartz chips (contact time, ~2 min), clean fragmentation to tetralin (**2**) and methyl 2-deuteriovinyl ether (**3**) was observed. The aromatic hydrocarbon was isolated by preparative scale vpc for the purpose of unequivocal identification. Ether **3** was transferred on a high vacuum line to an nmr tube containing $CDCl_3$–TMS. The relative proportions of cis and trans isomers were then established by quantitative integration of expanded scale nmr spectra taken at 100 MHz. The results are summarized in Table I. Control experiments with unlabeled propelladienes have confirmed that syn–anti interconversion of the methoxyl group is not operative under the conditions of thermal activation. The geometric isomers of **3** also have been shown to be stable at these temperatures.



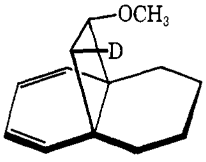
1 2 **3a**, *cis* **b**, *trans*

Table I. Thermally Generated Isomer Distributions of **3**

Reactant	*T*, °C	Rel % yield 3a	Rel % yield 3b
1	245	98	2
	314	97	3
4	245	80	20
	314	77	23
1 + **5**[a]	314	29	71

[a] The **1**:**5** ratio was 26:74.

The thermal cycloreversions of anti,cis isomer **4**[5] and syn,trans isomer **5**[5,6] have likewise been investigated.



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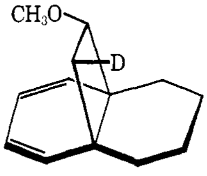
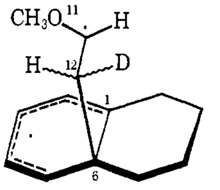


5

The data of Table I reveal that although propelladiene **4** exhibits formally only a 79% preference for the $[_\sigma 2_s + {}_\sigma 2_s]$ pathway, isomers **1** and **5** are subject to cleavage with exceptionally high levels of double retention. In the latter two cases, irreversible cleavage of the C_6–C_{12} bond in diradical **6**[7] to produce tetralin is evidently much faster than C_{11}–C_{12} bond rotation. Although such evidence may appear to support the twixtyl concept, two important factors can otherwise account satisfactorily for the high k_{scis}/k_{rot} ratio observed with **1** and **5**. Firstly, C_{11}–C_{12} bond rotation would require the methoxy group to migrate from a site over the diene unit where it is sterically unencumbered to a position over the tetramethylene bridge where serious compression with the axially disposed methylene hydrogens will be engendered. The untoward effect of such nonbonded repulsive interactions is certain to be energetically unrewarding. Secondly, the methoxyl group is a rather massive rotor and a bias in favor of k_{scis} should be accentuated by the sheer ponderal effect associated with this type of substitution.[8]



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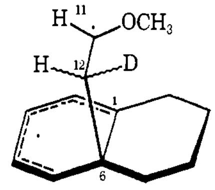
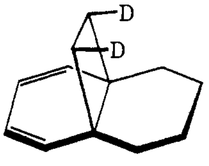


7

The purely steric considerations would appear to be supported by the behavior of **4**. Initial rupture of the C_1–C_{11} bond in this example leads initially to **7** in which the methoxyl substituent is constrained into space occupied by at least one axial hydrogen. Bond rotation in the 1,4 diradical to arrive at thermodynamically more favorable conformation **6** now becomes reasonably competitive with k_{scis}. The partial loss of stereochemistry attending the cycloreversion of **4**, particularly as it contrasts with the stereoselectivity exhibited by **1** and **5**, is qualitatively concordant with this analysis.



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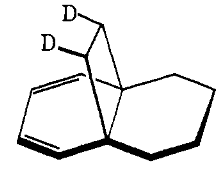

9

To gain information on the importance of ponderal effects as they relate to increased rotational barriers in these systems, the pyrolysis of **8** and **9** has been examined. Although our synthesis of these 11,12-*cis*-dideuteriopropelladienes resulted inevitably in the simultaneous production of **8** and **9** (ratio 3:2), the reaction of major interest was that leading to the 1,2-dideuterioethylenes. Pyrolyses at 310° as before were again uncomplicated by side reactions. Isolation of the ethylenes and analysis of the relative proportion of geometric isomers were performed as described in the ensuing communication.[9] The relative intensities of the nmr absorptions indicated that the amount of cis isomer produced was 66 ± 1%. The striking feature of these results is the obviously low stereoselectivity. Although the predominant course of the cycloreversion occurs in a stereochemical sense compatible with $k_{scis} > k_{rot}$, such $[_\sigma 2_s + {}_\sigma 2_s]$ elimination of ethylene is only marginally favored. Rather, it

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(6) The synthetic method employed in the preparation of **5** provided material of 74% geometric purity. The minor isomer was **1** (26%). Because of the high level of stereoselectivity observed in the fragmentation of **1**, proper normalizations can be applied to the data derived from the pyrolysis of this mixture in order to delineate the stereochemical course of the cycloreversion exhibited by **5**.

(7) Since the activation energies associated with homolytic reactions are recognized to differ principally by the resonance energies developed in their biradicals, bond rupture in the 11-methoxypropelladienes is expected to occur first at C_1–C_{11}. For further discussion of this point, see ref 4b and D. A. Bittker and W. D. Walters, *J. Amer. Chem. Soc.*, **77**, 1429 (1955).

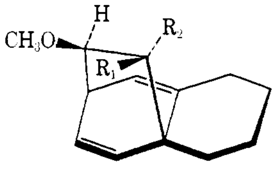
(8) Ponderal and energetic effects as they apply to 1,4 diradicals have previously been discussed: J. A. Berson, D. C. Tompkins, and G. Jones, II, *ibid.*, **92**, 5799 (1970).

(9) L. A. Paquette and L. M. Leichter, *ibid.*, **93**, 4922 (1971).

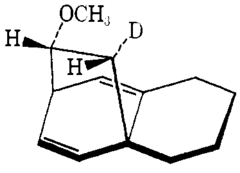
would appear that bond rotation and cleavage compete quite favorably. On this basis, the high levels of preservation of geometrical relationships which are evidenced in the thermolysis of **1** and **5** can be attributed in large measure to increased barriers to k_{rot} due to steric and ponderal factors. In the absence of at least one of these constraining features (*cf.* **4**, **8**, and **9**), 1,4-diradical intermediates exhibit little stereochemical preference. Such is not totally unexpected in view of the magnitude of the energy barrier associated with radical additions to benzene rings;[10] from microscopic reversibility considerations, there must exist a small but significant barrier for loss of a group from substituted cyclohexadienyl radicals.

Thus, loss of stereochemical integrity has been demonstrated for 1,4 diradicals in which k_{scis} has been appreciably enhanced relative to k_{rot}. We must therefore conclude that a singlet diradical of this type cannot accurately be described as a flat region atop an energy profile, *i.e.*, as a twixtyl. Instead the present results demand that those areas of potential energy space associated with semistabilized 1,4 radicals be more precisely characterized by maxima and minima which reflect such subtle intrinsic molecular features as steric demands and ponderal effects. This state of affairs would ensure significant passage of the reaction through the lowest energy conformation provided, of course, that the rates of ultimate bond scission for the various conformations are similar in magnitude. It may well be that under certain strictly specified conditions the diradical region will exhibit little deviation from the horizontal, but such twixtylic conditions need not always apply.

Finally, it should be noted that the available data do not rule out the possibility that portions of these fragmentations proceed by preliminary [1,3]sigmatropic rearrangement *via* intermediates of type **10** and subsequent stereospecific Diels–Alder fragmentation.[11] However, the high propensity of related dienes[12] for symmetry-allowed thermal [1,5]sigmatropic rearrangements suggests that this alternative does not gain importance.



10a, R$_1$ = D; R$_2$ = H
b, R$_1$ = H; R$_2$ = D



10c

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(10) M. Szwarc and J. H. Binks, *Theor. Org. Chem. Pap. Kekule Symp., 1958*, 263 (1959).

(11) It would have to be assumed that **1** and **5**, which both have *syn*-methoxyl groups, undergo this rearrangement with high retention of configuration to give **10a** and **10b**, respectively. In contrast, **4**, which has an *anti*-methoxyl group, would have to react with some inversion of configuration to provide the appropriate mixture of **10b** and **10c**. Alteration in the retention–inversion pathways of thermal [1,3]sigmatropic bicyclo[3.2.0]hept-2-ene rearrangements upon introduction of an added methyl group has been noted previously; J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **92**, 1096 (1970).

(12) (a) J. A. Berson and M. R. Wilcott, III, *ibid.*, **88**, 2494 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Wilcott, III, *ibid.*, **89**, 4076 (1967); (c) E. Ciganek, *ibid.*, **89**, 1458 (1967); (d) V. Rautenstrauch, H. J. Scholl, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 7, 288 (1968); (e) L. A. Paquette, D. E. Kuhla, and J. H. Barrett, *J. Org. Chem.*, **34**, 2879 (1969).

Acknowledgment. This research was supported in part through National Cancer Institute Grant No. CA 12115. The authors are also indebted to Professor G. Closs for the deuterium-decoupled nmr spectra and to Dr. Stanley A. Lang for assistance with the 100-MHz spectra.

(13) Philips Petroleum Fellow, 1970–1971; University Dissertation Fellow, 1971–1972.

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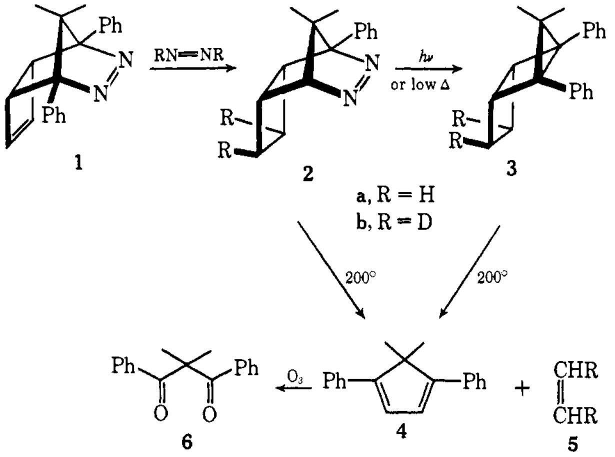
Pyrolysis of *anti*-Tricyclo[3.2.0.0^{2,4}]heptanes. The Role of 2,4 Substitution in the Operation of σ Bond Assisted Cyclobutane Fragmentations

Sir:

We wish to report discovery of the first example in which highly stereoselective cycloreversion of a cyclobutane to olefinic products according to the [${}_\sigma 2_s + {}_\sigma 2_s$] mode becomes energetically accessible and possibly concerted due to the suprafacial fragmentation of a third proximate σ bond. The resulting novel [${}_\sigma 2_s + {}_\sigma 2_s + {}_\sigma 2_s$] fragmentation follows a least motion path and contrasts with the severe distortions associated with the [${}_\sigma 2_a + {}_\sigma 2_s$] pathway otherwise demanded of concerted cyclobutane fragmentations.[1,2] The results to be described demonstrate that the proper juxtaposition of a relatively weak σ bond effectively obviates the necessity of twisting the four-membered ring at the transition state as well as the need for generating 1,4-diradical intermediates.

The synthetic scheme outlined below afforded a convenient route not only to **3a** but also to its 6,7-cis,exo dideuterio analog **3b**. Diimide readily (90%) reduced tricyclic azo compound **1**[3] to **2a**, mp 97–99° dec;[4] subsequent photolysis (100%, 200-W lamp, ether, Pyrex optics) or pyrolysis (>95%, 140°, 5 hr, CHCl$_3$) of **2a** gave **3a**, a colorless viscous oil.[4,5] An identical



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(1) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 65 ff.

(2) L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970), and pertinent references cited therein.

(3) L. A. Paquette and L. M. Leichter, *ibid.*, **92**, 1765 (1970); in press.

(4) Satisfactory spectral and analytical data were obtained for each new compound footnoted.

(5) For **3a**: $\delta_{\max}^{\mathrm{CDCl_3}}$ 7.67 (m, 10), 3.60 (m, 2), 1.82 (m, 4), 0.85 (s, 3), and 0.22 (s, 3). In **3b**, the multiplets at 3.60 and 1.82 are significantly sharpened and the 1.82 absorption displays a relative intensity of 2 H.