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ELECTROPHILIC SUBSTITUTION AND INTERNAL ROTATION IN ACYLPENTATRIAFULVALENES

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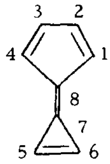
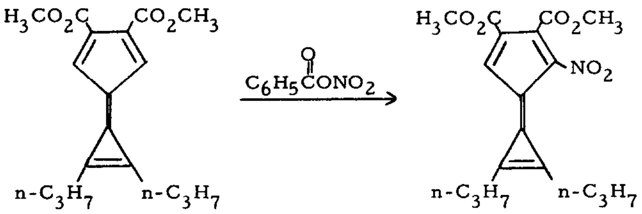
Recent LCAO-MO-SCF calculations by Dewar and Gleicher have led to the conclusion that the hydrocarbon pentatriafulvalene (I) is essentially a polyolefin possessing negligible resonance energy.[1]



(I)

The current availability of relatively simple acylpentatriafulvalenes from condensation of substituted cyclopentadienides with alkoxycyclopropenium salts[2,3] has permitted exploration of their behavior toward reagents known to effect electrophilic substitution of reactive aromatic subtrates. Our data indicate that acylpentatriafulvalenes undergo a wide range of electrophilic substitutions,[4] exemplified by the following reactions:

Nitration



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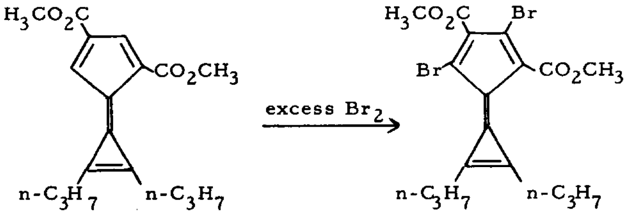
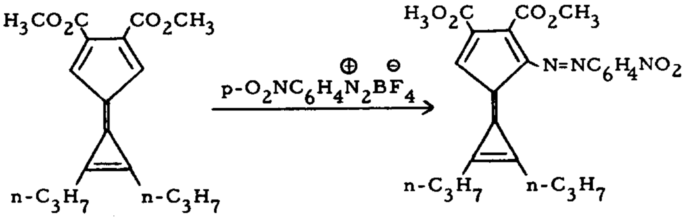
Bromination



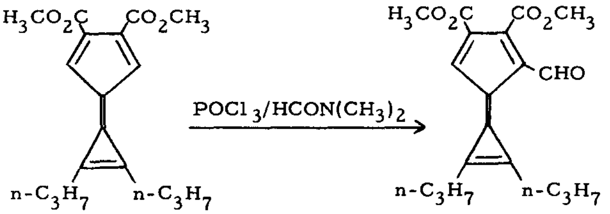
III

Azo-Coupling



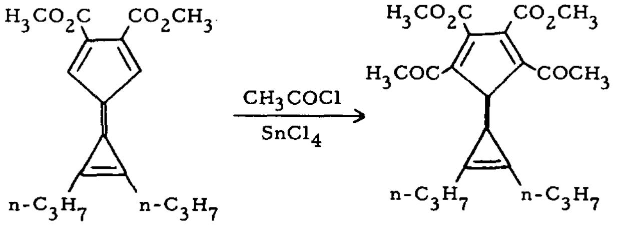
IV

Vilsmeier - Haack Formylation



V

Friedel-Crafts Acetylation



VI

Retention of the pentatriafulvalene system in these reactions was demonstrated in each case by the characteristic infrared maxima near 5.4, 6.6 and 6.8 u, and by analytical, n.m.r. and ultraviolet spectroscopic characterization of the products (Table I). It is noteworthy that simple fulvenes and acylfulvenes normally undergo addition or polymerization rather than substitution under these conditions.[5]

TABLE I

Electrophilic Substitution Products[6]

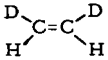
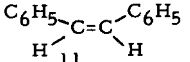
Compound	M. p.	UVλ_{max} (logϵ)	%C	%H	Ring H (n. m. r.)
II	133-134°	380(3.93),340(3.87) 279(4.38), 225(4.00)	61.86	5.87	2.82τ(1H, singlet)
III	131-132°	340(4.62), 260(4.45)	Br = 34.96		none
IV	122-124	450(4.20), 292(4.39)	63.46	5.90	2.72τ(1H, singlet)
V	95-96°	345(4.16), 325 sh 272(4.55), 228(4.02)	69.28	6.90	2.66τ(1H, singlet)
VI	167-168°	348(4.07), 275(4.33)	68.73	7.25	none

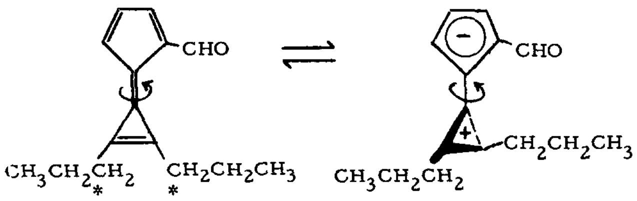
Our observations do not necessarily inweigh against the conclusions of Dewar and Gleicher based on pentatriafulvalene itself, since any electron-withdrawing group in the five-membered ring should increase its cyclopentadienide character relative to the parent hydrocarbon. One result of such electron transfer would be a lowering of the double-bond character of the intercyclic 7, 8-bond. Direct evidence bearing on this matter is now available from variable temperature studies of the 60 mc. n. m. r. signals of α-methylene groups (starred in formula VII) of the stable aldehyde VII.[7] At room temperature the two magnetically dissimilar methylene groups show a pair of triplets separated by a chemical shift difference ν_A-ν_B ranging from 7 to 39 c. p. s., depending on solvent (Table II). Increase in temperature results in coalescence of the broadened α-methylene signals; further heating finally generates a lone triplet located halfway between ν_A and ν_B.[8] This phenomenon is characteristic of rapid exchange between two equally populated sites and in this instance presumably arises from internal rotation about the C(7)-C(8) bond. From the relation[9] $k_1 = \pi(\nu_A - \nu_B)/\sqrt{2}$ the rate constant k_1 at coalescence temperature T_c can be obtained, and thence the corresponding value for the free energy of activation $\Delta F^{\ddagger}$ can be derived from the Eyring equation by assuming a unit transmission coefficient.

TABLE II

Kinetic Parameters for Internal Rotation in Aldehyde VII

Solvent	Dielectric Constant	$\nu_A - \nu_B$ (c.p.s.)	T_c	k_1 (sec.$^{-1}$)	$\Delta F^{\ddagger}$ (kcal./mole)
$(C_6H_5)_2O$	4	39.0	387±3°	86.6	19.4±0.4
o-$C_6H_4Cl_2$	10	28.5	378±3	63.3	19.2±0.4
C_6H_5CN	26	18.0	356±3	40.0	18.4±0.4
$HCON(CH_3)_2$	38	7.3	339±3	16.2	18.0±0.4

In the light of reported values for thermal cis-trans isomerizations of  $\mathrm{DHC{=}CHD}$ and  $\mathrm{C_6H_5HC{=}CHC_6H_5}$ of $\Delta F^{\ddagger}$ = 65 kcal. per mole[10] and 44 kcal. per mole,[11] respectively, our figure of ca. 19 kcal. per mole corresponds to an abnormally low rotational barrier and presumably a low bond order for the intercyclic bond in aldehyde VII. The modest but consistent decrease in the rotational barrier with increase in solvent dielectric constant implies that rotation proceeds through a transition state more polar than the ground state. It is tempting to propose that the transition state consists of a cyclopropenium cation and a cyclopentadienide anion at 90° angles to each other (*cf.* VIII).



VII VIII

The observed electrophilic reactivity and facile internal rotation of acylpentatriafulvalenes are consistent with a significant measure of cyclopropenium-cyclopentadienide "aromaticity" in these systems.

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4. High reactivity of the pentatriafulvalene system toward electrophiles has been predicted by the SCF localization energy calculations of O. Chalvet, R. Daudel and J. J. Kaufman, *J. Chem. Phys.* **68**, 490 (1964). This type of calculation can not predict whether addition or substitution will follow such electrophile attack.
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6. We are indebted to L. Brancone and his associates for the microanalytical data reported here.
7. The synthesis and detailed characterization of this compound (m.p. 64-65°), prepared from sodium formylcyclopentadienide and 1-ethoxy-2,3-di-n-propylcyclopropenium tetrafluoroborate, are described elsewhere.[2]
8. Appropriate controls were run to demonstrate the stability of compound VII during the n.m.r. experiments.
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