cyclooctane provides a satisfactory quantitative explanation for previously puzzling proton spin–echo measurements on this compound.[9] It also supports a new rationalization[2g] of the low-temperature ^{19}F nmr spectrum of 1,1,2,2-tetrafluorocyclooctane,[2c,10] based on a 1:1 mixture of boat–chair and twist-chair–chair conformations. The fact that I exists predominantly in the twist-chair–chair with one vicinal pair of bromines diequatorial and the other diaxial is probably a result of repulsions in the boat–chair, where all the bromines are equatorial,[11,12] although other effects[13] may also be important.

Acknowledgment. This work was supported by the National Science Foundation.

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[9] S. Meiboom, paper presented at the Symposium on High Resolution Nuclear Magnetic Resonance at Boulder, Colo., July 1962. The existence in cyclooctane of two distinct T_2 effects in the range of −50 to −100° was established and thought to be due to a partial averaging of chemical shifts in a single conformation. This interpretation is in conflict with other nmr evidence,[2] however, and we have recently suggested that the spin–echo results could be explained if a small amount of a crown family conformation coexisted with the boat–chair.[2g]

[10] The original explanation[2c] was based on a 1:1 mixture of two different twist-boats.

[11] *trans*-1,2-Dibromocyclohexane exists preferentially in the diaxial conformation.[12]

[12] F. R. Jensen and C. H. Bushweller, *Advan. Alicycl. Chem.*, 3, 139 (1971).

[13] *trans*-1,4-Dibromo- (or dichloro-) cyclohexane exists to a much greater extent in the diaxial form than expected from a simple additivity of *A* value;[12] see also R. J. Abraham and Z. L. Rossetti, *Tetrahedron Lett.*, 4965 (1972).

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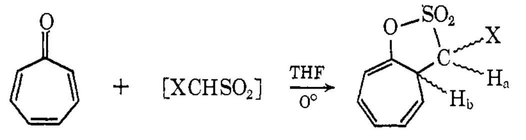
Stereoselective Sulfene–Tropone Cycloadditions and Stereospecific Thermolysis of Resulting Adducts

Sir:

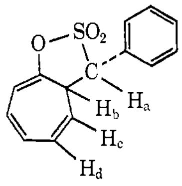
Several sulfenes have been found to cycloadd to tropone in a highly stereoselective fashion to form the corresponding γ-sultones[1] (eq 1 and Table I). A



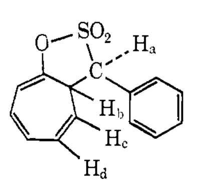
(1)

solution of freshly distilled triethylamine (0.005 mol) in anhydrous tetrahydrofuran was added dropwise (over a 2–3 hr period) to a stirred solution of tropone (0.005 mol) and α-toluenesulfonyl chloride (0.005 mol) in anhydrous tetrahydrofuran at 0° under nitrogen. Filtration of triethylamine hydrochloride and removal of tetrahydrofuran *in vacuo* gave a brown oily residue, which solidified in absolute ethanol at ice bath temperature. Recrystallization from absolute ethanol gave a white crystalline solid in good yield, mp 139–140°. *Anal.* Calcd for $C_{14}H_{12}SO_3$: C, 64.61; H, 4.62; S, 12.31; mol wt, 260. Found: C, 64.34; H, 4.79; S, 12.58; mol wt (osmometer), 262.7. Mass spectra data: *m/e* 260, 196, 181, 178, 177, 176, 167, 165. Ir (Nujol, μ): 6.05, 7.31, 8.28, 8.7, 9.08, 12.0, 12.85, 13.45, 13.98. Nmr (60 Mc, $CDCl_3$–TMS, δ): 3.5–3.8 (1 H, complex multiplet), 4.7–4.95 (2 H, doublet overlapping double doublet), 5.9–6.3 (2 H, complex multiplet), 6.3–6.5 (2 H, complex multiplet), 7.40 (5 H, s).

All of the above data are clearly consistent with a one to one sulfene–tropone adduct, either IIa or IIb.



IIa cis



IIb trans

Investigation of the nmr spectrum using double resonance further supports structure II. Irradiation at δ 3.67 (H_b) collapses the doublet at δ 4.9 (H_a) to a singlet and the double doublet at δ 4.8 (H_c) to a doublet (J_{ab} = 9 cps, J_{bc} = 4 cps, J_{cd} = 9 cps).

Treatment of the initial adduct with base yielded a new compound, mp 126–127°, believed to be the geometric isomer of the initial adduct. *Anal.* Calcd for $C_{14}H_{12}SO_3$: C, 64.61; H, 4.62; S, 12.31; mol wt, 260. Found: C, 64.75; H, 4.86; S, 12.14; mol wt (osmometer), 260.2. Ir (Nujol, μ): C, 6.02, 7.31, 8.28, 8.90, 11.90, 12.30, 12.8, 14.1, 14.4. Nmr (60 Mc, $CDCl_3$–TMS, δ): 3.4–3.55 (1 H, complex multiplet), 4.72 (1 H, doublet), 5.0–5.3 (1 H double doublet), 6.0–6.6 (4 H, complex multiplet), 7.42 (5 H, s) (J_{ab} = 9 cps, J_{bc} = 4 cps, J_{cd} = 9 cps). Mass spectral data: *m/e* 260, 196, 181, 178, 177, 176, 167, 165.

Different chemical shifts in the nmr (but with identical splitting patterns), similar ir data, nearly identical mass spectra, and satisfactory elemental analysis data establish that the second compound is the stereoisomer of the initial adduct, *i.e.*, IIa and IIb are cis–trans isomers. Furthermore, thermolysis of the adducts (eq 2 and 3 and Table I) and other analogous reactions show that the initial adduct is the cis isomer.

It is striking that we were unable to detect the trans adduct in any of the unpurified reaction mixtures. All initial adducts appear in the nmr to be the cis isomer. The fact that "X" is in every case capable of bearing substantial negative charge might indicate that Coulombic attractions between the tropylium cation and the negatively charged "X" group leads to preferential collapse of a zwitterionic intermediate[1] to cis product without competition between bond rotations and ring closure. A thermally allowed [$_\pi 8_s + _\pi 2_s$] cycloaddition would just as well explain the great stereoselectivity.

When these sulfene–tropone adducts (γ-sultones) are heated, they undergo a novel thermodecomposition with loss of sulfur dioxide to yield stilbene or styrene derivatives in a highly stereospecific manner (eq 2 and 3). The cis sulfene–tropone adduct (IIa, X = C_6H_5, mp 139–140°) was dissolved in dioxane (or DMSO, dioxane–water, THF) and heated to about

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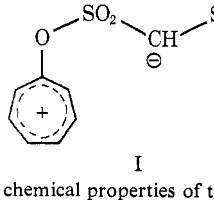
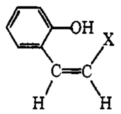
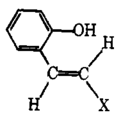
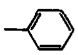
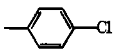
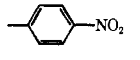
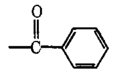
[1] J. Ciabattoni and M. Cabell, *Tetrahedron Lett.*, 2693 (1968), reported a two to one adduct of sulfene and tropone, which was interpreted to arise *via* a dipolar intermediate, I. Neither the stereochemistry of



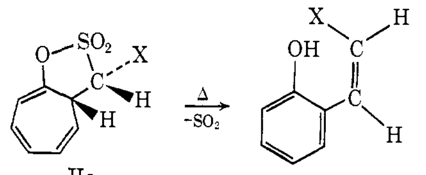
I

the reaction nor the chemical properties of the product were discussed.

Table I

X	Mp, °C, cis	Mp, °C, trans	Yield,[a] %	J_{ab}, cps (cis)	J_{ab}, cps (trans)	Bp of 	Mp of 
	139–140	126–127	95	9	9	108–110° (0.1 mm)	143–144°
	138–139	99–100	86	9	8.5	124–125° (0.2 mm)	122–123°
	143–144	127–128	>40[b]	9	7	High boiling	187° dec
	*c*	131–133	85	9	6		153° dec
-CN	*d*	*d*	92	9.5	6.5	*e*	126–127°
$-SO_2CH_3$	*c*	157–159	88	9	5.3		136–137.5°
$-CH{=}CH_2$	62.5–63.5	*f*	82	8.5		*g*	5–7°

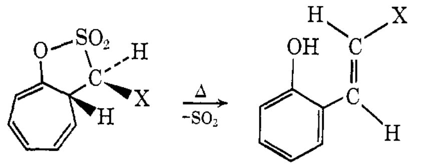
[a] For initial adduct, based on tropone conversion. [b] Forty per cent would be based on complete conversion of tropone. [c] Isomerized during work-up. [d] High boiling oil, decomposed at high temperature, isomerized to a 50:50 cis:trans mixture in a silica gel column. [e] Coumarin was isolated (see eq 7). [f] An equilibrium mixture when tried to isomerize by base. [g] VII was isolated (see eq 8).



IIa IIIa (2)

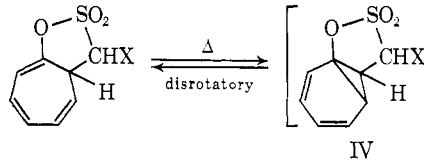
90° for 6–10 hr. Removal of solvent gave a clean oily residue (bp 108–110° (0.1 mm)) in approximately 90% yield. *Anal.* Calcd for $C_{14}H_{12}O$: C, 85.67; H, 6.17; mol wt, 196. Found: C, 85.76; H, 5.94; mol wt (osmometer), 193.2. Mass spectral data: *m/e* 196, 195, 181, 179, 178, 168, 167, 166, 165. Ir (neat, μ) 2.8–2.9 (broad), 6.20, 6.31, 6.7, 6.9, 7.5, 7.9, 8.3–8.5 (broad), 9.15, 12.0, 12.8, 13.3, 14.4. Nmr ($CDCl_3$–TMS, δ): 5.0 (1 H, broad), 6.4–6.8 (2 H, AB quartet, J_{ab} = 12 cps), 6.8–7.2 (4 H, complex multiplet), 7.19 (5 H, s). Uv $\lambda_{max}^{CH_3OH}$ (nm) 277 (log ε 3.95), 3.05 (log ε 3.85). All of the above data are clearly consistent with *cis*-2-hydroxystilbene (IIIa).

Extrusion of sulfur dioxide from the trans adduct of phenylsulfene and tropone (eq 3, IIb, X = C_6H_5, mp 126–127°) in a similar fashion yielded a solid product. Recrystallization from chloroform gave white crystals, mp 143–144°, in 86% yield. *Anal.* Calcd for $C_{14}H_{12}O$: C, 85.67; H, 6.17; mol wt, 196. Found: C, 85.51; H, 6.20; mol wt (osmometer) 195.5. Mass spectral data: *m/e* 196, 195, 181, 179, 178, 177, 168, 167, 166, 165. Ir (Nujol, μ): 2.80 (sharp), 6.30, 6.90, 7.50, 8.10, 8.35, 9.18, 10.20, 11.80, 13.20, 14.45. Nmr ($CDCl_3$–TMS, δ): 5.2 (1 H, broad), 6.6–7.2 (11 H, complex multiplet, in pyr-d_5–$CDCl_3$, one-half of an AB quartet with J_{ab} = 16.5 cps is visible). Uv $\lambda_{max}^{CH_3OH}$ (nm): 286 (log ε 4.14), 297 (log ε 4.12), 317 (log ε 4.10).

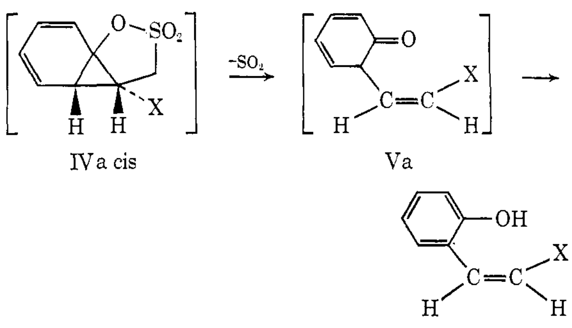


IIb IIIb (3)

Again, these data are consistent with *trans*-2-hydroxystilbene (IIIb) (lit.[2] for 2-hydroxystilbene of unspecified configuration, mp 145°). Hydrogenation of the two isomers (IIIa and IIIb) gave the same compound, 2-hydroxybibenzyl, mp 82–83.5° (lit.[3] mp 84–85°). The cis adducts gave *cis*-stilbene (styrene) derivatives and trans adducts gave *trans*-stilbene (styrene) derivatives stereospecifically (Table I). The triene system in the adduct probably closes in a thermally allowed disrotatory (4*n* + 2)π manner to give tricyclic intermediates (IV). These intermediates, however, are unstable at this temperature and subsequently lose SO_2 in a ($_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s$) process. Such processes are analogous to the retrohomo-Diels–Alder[4] reaction. It has been observed that the cyclopropane ring can play the same role as a π bond.[4] The cyclopropane ring in our tricyclic intermediate may play the same role, undergoing a thermally allowed ($_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s$) process to give V in a stereospecific manner. Intermediates V then undergo enolization to give final products (eq 5 and 6). An interesting modification



IV (4)



IVa cis Va

cis (5)

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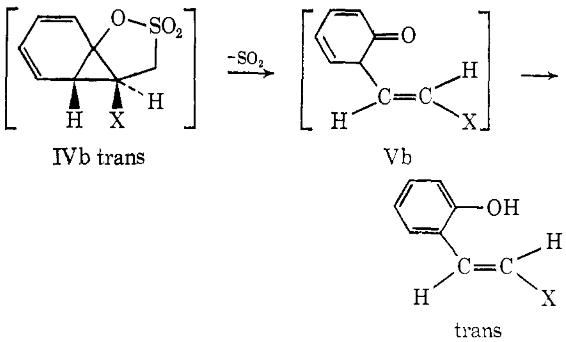
[2] von Hugo Kauffmann, *Justus Liebigs Ann. Chem.*, **433**, 237 (1923); St. v. Kostanecki and J. Tambor, *Chem. Ber.*, **42**, 826 (1909).

[3] R. Stoemer, *Chem. Ber.*, **36**, 3982 (1903); O. Kippe, *ibid.*, **36**, 4007 (1903); P. Schorigin, *ibid.*, **58**, 2032, 2033 (1925).

[4] T. L. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry," Cambridge University Press, London, 1972, pp 106–109.



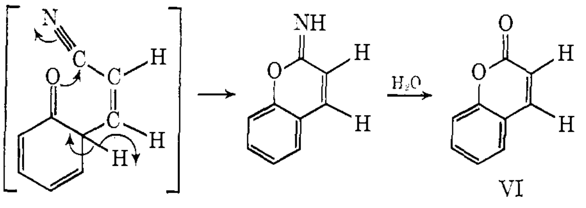
IVb trans

Vb

trans

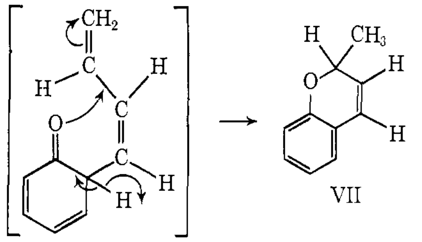
(6)

in reaction path occurs when "X" in Va is -CN or -CH=CH$_2$; subsequent cyclization yields VI and VII (eq 7 and 8).



(7)

VI



(8)

VII

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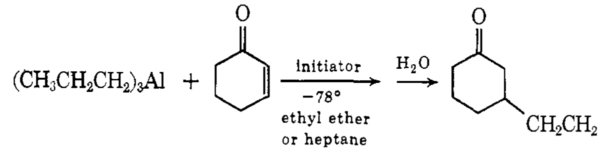
Received February 14, 1973

Reaction of Tri-*n*-propylaluminum with α,β-Unsaturated Ketones. Evidence for a Free-Radical Chain Mechanism

Sir:

We wish to report the first unequivocal example of a free-radical chain reaction involving trialkylaluminum compounds. Tri-*n*-propylaluminum reacts readily with α,β-unsaturated ketones in the presence of radical initiators at −78° producing the conjugate addition products exclusively. In the absence of free-radical initiators, no reaction occurs. The reaction is exemplified by the synthesis of 3-*n*-propylcyclohexanone (eq 1).



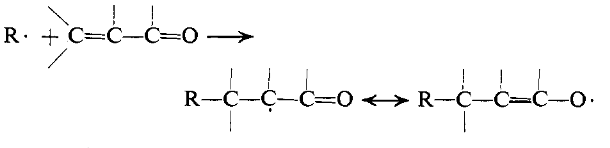
$$(CH_3CH_2CH_2)_3Al + \text{2-cyclohexenone} \xrightarrow[\text{ethyl ether or heptane}]{\text{initiator, } -78^\circ} \xrightarrow{H_2O} \text{3-}(CH_2CH_2CH_3)\text{cyclohexanone} \qquad (1)$$

There has been a great deal of interest in recent years focused on the free-radical reactions of organometallic compounds. Excellent reviews on this subject have recently appeared.[1,2] It is known that an S$_H$2 process can occur readily at an aluminum center (eq 2).[3,4] If

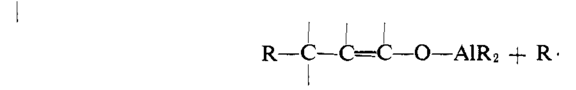
$$R'O\cdot + R_3Al \longrightarrow R'OAlR_2 + R\cdot \qquad (2)$$

the alkyl radical thus produced could be caused to regenerate an alkoxy radical, a chain process would result. This has been demonstrated to be the case for the autoxidation of organoboranes and alkyltin chlorides[5] as well as for the 1,4-addition reactions of organoboranes.[6] It has been postulated that the autoxidation of organoaluminum compounds proceeds *via* a free-radical chain reaction but the evidence is not compelling.[7]

In view of our recent studies on the free-radical reactions of organoboranes, it seemed reasonable to expect that a trialkylaluminum compound would undergo an analogous free-radical chain reaction with an α,β-unsaturated carbonyl compound (eq 3 and 4).[6,8]



$$R\cdot + {>}C{=}C{-}C{=}O \longrightarrow R{-}C{-}\dot{C}{-}C{=}O \longleftrightarrow R{-}C{-}C{=}C{-}O\cdot \qquad (3)$$



$$R{-}C{-}C{=}C{-}O\cdot + R_3Al \longrightarrow R{-}C{-}C{=}C{-}O{-}AlR_2 + R\cdot \qquad (4)$$

Previous attempts to achieve the conjugate addition of trialkylaluminum compounds to α,β-unsaturated systems had been unsuccessful,[9] generally leading to polymerization[10] or 1,2-addition products.[11,12] It appeared likely that the carbonyl addition reaction could be eliminated simply by lowering the reaction temperature to take advantage of the relatively high E_A of this process (approximately 19 kcal/mol).[13]

We have found this to be the case. Tri-*n*-propylaluminum does not react with 2-cyclohexenone at −78° in alkane or ether solvents even after a period of 30 hr.[14] However, in the presence of radicals generated by irradiation, a 75% yield of 3-*n*-propylcyclo-

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(1) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-International, New York, N. Y., 1971.

(2) A. G. Davies and B. P. Roberts, *Accounts Chem. Res.*, **5**, 387 (1972).

(3) A. G. Davies and B. P. Roberts, *J. Organometal. Chem.*, **19**, P17 (1969).

(4) P. J. Krusic and J. L. Kochi, *J. Amer. Chem. Soc.*, **91**, 3942 (1969).

(5) A. G. Davies, T. Maki, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 744 (1972).

(6) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, **92**, 710 (1970).

(7) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 1074 (1968).

(8) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **93**, 1024 (1971).

(9) (a) Although no successful 1,4-addition reactions of trialkylaluminum reagents have been achieved, H. Gilman and R. Kirby did achieve the 1,4 addition of triphenylaluminum to benzalacetophenone [*J. Amer. Chem. Soc.*, **63**, 2046 (1941)]. (b) A successful 1,4-addition reaction of trialkylaluminum reagents was reported by Y. Kawakami [*J. Macromol. Sci. Chem. A*, **3** (2), 205 (1969)]. Our attempts to reproduce the reported reactions under the conditions described lead to quantitative 1,2 addition of the organoaluminum reagent to the carbonyl group.

(10) T. Tsuruta, R. Fujio, and J. Fumkawa, *Macromol. Chem.*, **80**, 172 (1964).

(11) Y. Baba, *Bull. Chem. Soc. Jap.*, **41**, 928 (1968).

(12) A. R. Lyons and E. Catterall, *J. Organometal. Chem.*, **25**, 351 (1970).

(13) E. C. Ashby, S. Yu, and P. Roling, *J. Org. Chem.*, **37**, 1918 (1972).

(14) Tri-*n*-propylaluminum was added to an equimolar quantity of 2-cyclohexenone in ethyl ether (temperature maintained at −78°). After 30 hr, the mixture was hydrolyzed. Glpc analysis indicated quantitative recovery of 2-cyclohexenone. Similar results were obtained utilizing 3-penten-2-one.