An ir spectrum (KBr) exhibited absorptions at 3110 (w), 2000 (s), 1925 (s), 1100 (w), 1100 (m), 1030 (m), 840–880 (m, br), 690 (w), 660 (s), and 635 cm^{-1} (s). An nmr spectrum exhibited a multiplet at τ 5.03 (two α protons on cymantrene ring), a multiplet at 5.24 (two β protons on cymantrene ring), a multiplet at 5.60 (two α protons on ferrocene ring), a multiplet at 5.70 (two β protons on ferrocene ring), and a singlet at 5.87 (five protons on unsubstituted ferrocene ring).

Elution of band III and subsequent evaporation of the solvent afforded 640 mg of (fulvalene)hexacarbonyldimanganese (1), identified by its ir spectrum.

Acetylation of (Fulvalene)hexacarbonyldimanganese (1).—A 100-ml three-necked flask was equipped with a magnetic stirrer, condenser, and a nitrogen inlet tube. To this flask was added 0.5 g (1.2 mmol) of (fulvalene)hexacarbonyldimanganese dissolved in 25 ml of dry methylene chloride, followed by 0.16 g (2.5 mmol) of acetyl chloride and 0.33 g (2.5 mmol) of aluminum chloride. The solution was heated to reflux under nitrogen for 30 min after which time it was poured over 50 g of ice. The organic layer was separated, dried over calcium chloride, and evaporated to dryness. The remaining residue was then subjected to preparative tlc (elution with methylene chloride). Development of the plate yielded three major bands.

Extraction of band I (highest R_f) from the plate and subsequent evaporation of the solvent yielded 0.12 g of unreacted 1, mp 146–147°. Band II was extracted from the plate and the solvent evaporated *in vacuo*. Sublimation of the residue which remained at 120° (0.01 mm) produced 0.24 g (43%) of (3-acetylfulvalene)-hexacarbonyldimanganese (11), mp 116.0–116.5°, as yellow platelets.

Anal. Calcd for $C_{18}H_{10}Mn_2O_7$: C, 48.25; H, 2.25. Found: C, 48.27; H, 2.44.

An ir spectrum (KBr) exhibited absorptions at 2020 (sh), 2000 (s), 1965 (s), 1935 (s), 1915 (s), 1680 (m), 1460 (w), 1425 (w), 1365 (w), 1240 (w), and 620 cm^{-1} (s). An nmr spectrum exhibited a multiplet at τ 4.30 (one proton α to both the acetyl group and the ring junction), a multiplet at 4.50 (one proton α to acetyl group and β to ring junction), a multiplet at 4.92 (three protons; one proton β to acetyl group and α to bridging carbon plus two protons α to bridging carbon), a multiplet at 5.16 (two protons β to bridging carbon), and a singlet at 7.64 (three protons of the acetyl group).

Band III yielded a product tentatively identified as an additional acetylation product of 1. An ir spectrum of the product (KBr) exhibited strong absorptions at 2020, 1970, and 1680 cm^{-1}.

Registry No.—**1**, 31988-02-0; **2**, 12079-65-1; **3**, 12203-10-0; **4**, 12079-63-9; **5**, 12216-27-2; **6**, 37048-11-6; **7**, 1274-09-5; **8**, 38855-99-1; **10**, 38856-00-7; **11**, 38856-01-8; cobalt(II) chloride, 7646-79-9.

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Semiempirical Calculations on the Ring Opening of Substituted Cyclopropanones

A. LIBERLES,* S. KANG, AND A. GREENBERG

Departments of Chemistry, Fairleigh Dickinson University, Teaneck, New Jersey 07666,[1] Frostburg State College, Frostburg, Maryland 21532, and the Department of Pharmacology, Mount Sinai School of Medicine, New York 10029, New York

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We report the results of INDO and MINDO calculations on the ring openings of cyclopropanone and some of its derivatives and compare the semiempirical results for the parent compound with the *ab initio* results reported earlier. Both semiempirical methods indicate that the substituted cyclopropanones open more readily than the parent compound, but the actual numerical values are not accurate. The major shortcoming of the semiempirical methods is that one never knows when to believe their predictions.

A large number of successful applications of the INDO and MINDO methods have been reported.[2–5] However, in a semiempirical approach the parameters are either not sufficiently flexible or not sufficiently accurate, and examples are bound to exist where these methods fail. It has already been reported that the ring opening of cyclopropanone **1** to singlet oxyallyl **2** is

1 **2**

such a case.[6] The INDO method predicts a value in excess of 200 kcal/mol, which is certainly too large.[6,7] The MINDO method has been reported to yield a more reasonable value, 78 kcal/mol, for the isomerization.[5] However, as we shall see, this method also fails in several substituted cases, predicting that the corresponding oxyallyls are considerably more stable. An extended Hückel study on the parent system also predicts oxyallyl to be more stable than cyclopropanone,[8] a result now known to be incorrect.[9,10]

An *ab initio* study indicates that singlet oxyallyl is 83 kcal/mol less stable than the closed ketone.[7] Because it does not include correlation, this value is probably too high.

Even allowing for some decrease, the energy difference between **1** and **2** is likely to remain large; yet, in contrast to the parent compound, some derivatives of **1** undergo reactions best explained in terms of an oxyallyl intermediate.[11–16] Concerted reactions need not pass

(1) Address for correspondence.

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through a true oxyallyl, but a number of reactions remain that do seem to require an oxyallyl. Therefore, these substituted oxyallyls must be formed much more readily than the parent molecule. For example, it has been reported that the racemization of optically active *trans*-2,3-di-*tert*-butylcyclopropanone, which may proceed by way of the corresponding oxyallyl, has a free energy of activation of approximately 27 kcal/mol.[15] It, therefore, seemed quite a proper test of the semiempirical SCF methods to determine their predictions for the ring opening of substituted cyclopropanones.

Ring Opening of Cyclopropanone.—The ring opening of the parent system was first calculated using both the INDO and MINDO methods.[17] The energies of cyclopropanone, using several geometries, are presented in Table I.

TABLE I
THE ENERGY OF CYCLOPROPANONE

Ref	MINDO, eV	INDO, hartrees
a	−759.941	−41.028
b	−759.452	
c	−759.432	
d		−40.996

[a] The experimental geometry of Pochan, Baldwin, and Flygare; see ref 9 and 10. [b] The optimal geometry of Bodor, Dewar, Harget, and Haselbach. The CH_2 angle was 115°. See ref 5. [c] The optimal geometry of Bodor, Dewar, Harget, and Haselbach. The CH_2 angle was 120°. See ref 5. [d] The optimal geometry of Olsen, Kang, and Burnelle; see ref 6.

Apparently, the experimental geometry of Pochan, Baldwin, and Flygare[9,10] is nearly optimal both for the INDO approach and for our version of MINDO.[17] As shown in Table I, we did test the geometry reported to be optimal for MINDO,[5] but the experimental geometry gave a lower energy.

The energy of singlet oxyallyl **2** was next calculated for various internal C_3–C_1–C_2 angles, α. The results are given in Table II.

TABLE II
THE ENERGY OF OXYALLYL FOR VARIOUS INTERNAL ANGLES

α, deg	MINDO, eV	INDO, hartree[a]	INDO, hartree[b]
120	−756.888	−40.600	−40.618
110	−757.031	−40.616	−40.634
100	−757.187	−40.630	−40.647
90	−757.398	−40.640	−40.657
80	−757.753	−40.633	
70	−758.375	−40.535	

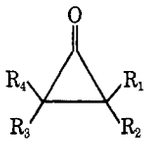
[a] Reference 6. [b] Present work; also see ref 7.

Oxyallyl is predicted by the INDO treatment to have an internal angle equal to 90°. The MINDO method indicates a smaller value for α. Unfortunately, the 60° geometry failed to converge with this method, and the 50° geometry places the endo hydrogens, H_2 and H_3, too close to be practical (d_{HH} = 0.0002 Å). Therefore, the smallest internal angle for which MINDO data are available is 70°.

Since the *ab initio* calculation[7] employed exactly the same bond distances as those used in the present work, it is possible to make a direct comparison of the predictions of the various methods. The INDO approach yields 232 kcal/mol for the ring opening and a value of 90° for α in oxyallyl. The *ab initio* result is 83 kcal/mol for the ring opening and approximately 105° for α. The MINDO method affords a value of 36 kcal/mol and α is in the neighborhood of 70°.[17]

A fuller optimization of the various structural parameters will somewhat change these values but not the conclusions.

Ring Opening of Substituted Cyclopropanones.—The substituted molecules **3** and **4** were derived from



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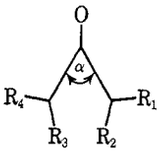

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the parent compounds by replacing hydrogens with the appropriate groups. An internal angle of 90° was chosen for the INDO calculations of the oxyallyls, while MINDO results were obtained for both 70 and 90°. The latter value allows a comparison of the two methods when identical bond distances and angles are employed.

Bond distances were obtained from model compounds,[18] and those used are shown in Table III. The

TABLE III
BOND DISTANCES IN SUBSTITUTED CYCLOPROPANONES AND OXYALLYLS

Substituent	3	4
F	1.350	1.340
CH_3	1.530	1.510
CH_3O	1.400	1.350
Methoxy CO	1.420	1.430
Methyl CH	1.100	1.100

energies for the isomerization are given in Table IV. We assumed that the opening of **3** was disrotatory, and of the two disrotatory modes, we chose the one placing bulky groups into positions R_1 and R_4.

The numerical values afforded by the two semiempirical methods are incorrect, but both methods do indicate that substituted cyclopropanones open more readily than the parent compound. The methoxy group, as expected, appears to be an extremely effective stabilizer of the ring-open form. Fluorine also appears to enhance the ring opening, but methyl is calculated to be less effective.

Conclusion

The data in Table IV support the idea that oxyallyls can be viable intermediates in the reactions of cyclopropanones, for both methods indicate that the substituted compounds open more readily than the parent molecule. Unfortunately, the actual numerical values are of little use. One method yields values that are much too large, while the other gives values that are obviously too low. The MINDO values for the parent system and its dimethyl derivative may not seem

(17) The version of MINDO used was QCPE 137, which uses different parameters from those of ref 5 and leads to different results.

(18) "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, Special Publications no. 11 and 18.

TABLE IV
THE ENERGY DIFFERENCE BETWEEN SUBSTITUTED OXYALLYLS AND THE CORRESPONDING CYCLOPROPANONES

					ΔE, kcal/mol		
Registry no.[b]	R_1	R_2	R_3	R_4	MINDO α 70°	MINDO α 90°	INDO α 90°
5009-27-8	H	H	H	H	+36	+59	+232
39050-15-2	F	H	H	F	a	+20	+184
39050-16-3	F	F	H	H	−153	+15	+203
39050-17-4	CH_3	H	H	CH_3	+30	+50	+200
39050-18-5	CH_3O	H	CH_3O	H	−93	+13	+180
39050-19-6	CH_3O	CH_3O	H	H	−96	+2	+174
39050-20-9	CH_3	F	F	CH_3	a	+14	+190
39050-21-0	CH_3O	F	CH_3O	F	−31	+24	+153
39050-22-1	CH_3O	CH_3O	F	F	−32	+30	+150

[a] The oxyallyl calculation failed to converge. [b] For cyclopropanones.

unreasonable, but the values for the fluoro and methoxy derivatives are incorrect, and the major shortcoming of the semiempirical methods is that one never knows when to believe their predictions.

Registry No.—Oxyallyl, 39050-23-2.

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Organic Reactions in Liquid Hydrogen Fluoride. IV.[1] The Fries Rearrangement of Aryl Benzoates

JOHN R. NORELL

Phillips Petroleum Company, Phillips Research Center, Bartlesville, Oklahoma 74004

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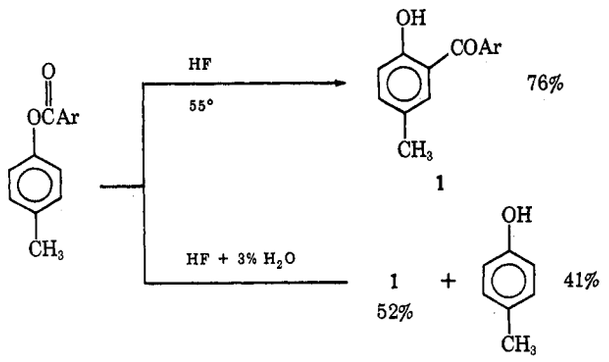
Phenyl and *p*-tolyl benzoates are converted to the corresponding hydroxybenzophenones in 70–75% yields when heated in anhydrous HF at 55°. With *p*-*tert*-butylphenyl benzoate the reaction product is the dealkylated *p*-hydroxybenzophenone, whereas the meta derivative gives 2-hydroxy-4-*tert*-butylbenzophenone in 40% yield. This appears to be the first example of a *tert*-butyl group being retained on a phenolic moiety during an acid-catalyzed Fries rearrangement. Comments on the mechanism and intermolecularity of the reaction are given.

Known as the Fries rearrangement,[2] the reaction of aryl esters in the presence of acidic type catalysts, usually $AlCl_3$, provides a convenient method for preparing hydroxybenzophenones. Hydrogen fluoride has received little attention as a catalyst for the rearrangement, although it has been reported to convert phenyl acetate[3] and some cresolic acetates[4] to the corresponding hydroxy ketones. The yields were low and a temperature of 100° for 24 hr was employed.[3] No work in HF has been reported with *tert*-butyl groups present on the phenolic ring; in fact, nothing in the literature could be found concerning favorable reactions with any *tert*-butylphenyl carboxylates employing any acid catalyst. Dealkylation always prevails, which led Kobsa[5a] to utilize the photo-Fries[5b] reaction for the rearrangement of *tert*-butyl esters.

Results

The present work describes our findings concerning rearrangement of some aryl benzoates in liquid HF, with special emphasis on the reactivity differences due to positions of *tert*-butyl groups on the phenolic ring. A summary of the experimental results is recorded in Table I. Phenyl and *p*-tolyl benzoate yield *p*-hydroxybenzophenone (70% yield) and 2-hydroxy-5-methylbenzophenone (76% yield), respectively, when shaken in liquid HF at 55° for 4–6 hr. The reaction is clean and the HF can easily be removed by distillation (bp 20°) or neutralization with base. No tars or insoluble residues often observed with $AlCl_3$ are obtained. If 3% water is present in the HF when *p*-tolyl benzoate is used as the starting ester, the isolated yield of ketone **1** drops to 52%, and 41% *p*-cresol is recovered resulting from hydrolytic cleavage of the ester.



p-Methoxyphenyl and *p*-chlorophenyl benzoates gave recovered starting material with *p*-methoxyphenol being obtained in the former case under the above con-

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