Lactone of 2-Carboxydiphenylferrocenylcarbinol. If the carbonation product from above was allowed to remain in contact with the hydrochloric acid used to acidify the solution, brown crystals were obtained upon evaporation of the solvent. Crystallization from ether produced a solid (40% yield) which melted sharply at 200°.

Anal. Calcd. for $C_{24}H_{18}FeO_2$: C, 73.12; H, 4.57; Fe, 14.17. Found: C, 73.06; H, 4.51; Fe, 14.00.

The infrared spectrum of this product showed unambiguous five-membered ring lactone absorption at 5.6 μ, and 9,10 μ ferrocene absorption. The spectrum was devoid of —OH absorption.

2-Methyldiphenylferrocenylcarbinol. Diphenylferrocenylcarbinol (30 g.; 0.08 mole) was metalated with *n*-butyllithium as described above. To this product was added 118 g. (0.8 mole) of dry methyl iodide in ether. After spontaneous reflux subsided, the mixture was refluxed under nitrogen for 24 hr. Hydrolysis with water was followed by separation and drying of the ether layer. Evaporation of the solvent, yielded 21 g. (69%) of amber crystals, which, after crystallization from ether, melted sharply at 167°.

Anal. Calcd. for $C_{24}H_{22}FeO$: C, 75.39; H, 5.80; Fe, 14.61. Found: C, 75.11; H, 5.81; Fe, 14.53.

The infrared spectrum of this material showed a strong —OH band at 2.8 μ, ring methyl absorption at 7.2 μ (absent in the spectrum of the parent carbinol), as well as the ferrocene absorption at 9 and 10 μ.

Ferrocenylphenyl-o-tolylcarbinol. *o*-tolyllithium was prepared by adding 85.5 g. (0.5 mole) of *o*-bromotoluene in 60 ml. of ether to 7.8 g. (1.2 g.-atoms) of lithium wire in ether under nitrogen. An ethereal solution of 18 g. (0.062 mole) of benzoylferrocene was added at a dropwise rate to the *o*-tolyllithium at room temperature. The mixture was stirred at room temperature for 24 hr. and then refluxed an additional 4 hr. After hydrolysis with water, the ether layer was separated and dried. Removal of the solvent deposited 18.0 g. (80%) of a yellow solid melting at 124–127°. This material was placed on an alumina chromatogram column, developed with benzene and eluted with ether. The analytical sample melted at 124–125°.

Anal. Calcd. for $C_{24}H_{22}FeO$: C, 75.39; H, 5.80; Fe, 14.61. Found: C, 75.59; H, 5.71; Fe, 14.83.

An infrared spectrum of this compound showed an —OH stretch at 2.9 μ, methyl compression modes at 6.9 μ (sym.) and 7.24 μ (antisym.) as well as the 9 and 10 μ peaks characteristic of ferrocene.

2-Hydroxymethyldiphenylferrocenylcarbinol. A 0.6-g. sample (0.0025 mole) of the pure lactone in ether was treated with an ethereal solution of 0.5 g. (0.013 mole) of lithium aluminum hydride under nitrogen. The amber solution rapidly changed into a yellow suspension accompanied by spontaneous reflux. When the reflux subsided, the mixture was refluxed for 24 hr. The excess hydride was destroyed with ethyl acetate and water was added. The ether layer was separated, and the solvent was removed under vacuum. A yellow solid (0.6 g.) was deposited melting in the crude state at 145°. After recrystallization from ether, the yellow crystals melted at 146°. The yield was quantitative.

Anal. Calcd. for $C_{24}H_{22}FeO_2$: C, 72.30; H, 5.55. Found: C, 72.16; H, 5.80.

The infrared spectrum of this material showed strong —OH absorption at 2.9 μ and the characteristic 9 μ and 10 μ bands of ferrocene.

bis-1,2-(Diphenylhydroxymethyl)ferrocene. Approximately 0.1 mole of phenyllithium in ether was added dropwise to an ethereal solution of 1.0 g. (0.0025 mole) of the lactone under nitrogen. Spontaneous refluxing occurred, followed by the formation of a yellow suspension. The mixture was stirred for 4 hr. at room temperature and then refluxed an additional 20 hr. After hydrolysis with water, followed by the usual work-up procedure a yield of 1.35 g. (97%) of a yellow solid melting at 190–192° was obtained. Recrystallization from ether yielded a dark yellow crystalline solid melting at 195–196°.

Anal. Calcd. for $C_{36}H_{30}FeO_2$: C, 78.55; H, 5.49; Fe, 10.15. Found: C, 78.31; H, 5.72; Fe, 9.97.

The infrared spectrum showed —OH absorption at 2.8 μ as well as the 9 and 10 μ bands of ferrocene.

p-Nitrobenzyl ester of 2-carboxyferrocenyldiphenylcarbinol. A 2.0-g. sample of the lactone (0.005 mole) was refluxed for 40 hr. in 100 ml. of 20% aqueous potassium hydroxide whereupon a brick-red suspension formed. The alkaline solution was neutralized to a *p*H of 7 with hydrochloric acid. Then a slurry of 3.0 g. (0.0175 mole) of *p*-nitrobenzyl chloride in 200 ml. of ethanol was added. The mixture was now refluxed for 24 hr. under nitrogen during which time a tan suspension formed. The mixture was filtered and the precipitate recrystallized from a large volume of ethanol producing 2.5 g. (93%) of a tan solid. This solid was triturated with tetrahydrofuran and filtered. The filtrate was evaporated. The residue was washed several times with ether and then recrystallized from acetone. It melted at 246°.

Anal. Calcd. for $C_{31}H_{25}FeNO_5$: C, 68.03; H, 4.58; N, 2.56; Fe 10.21. Found: C, 67.63; H, 4.81; N, 2.54; Fe, 10.27.

The infrared spectrum of this compound showed OH— absorption at 2.8 μ, carbonyl absorption at 5.85 μ, conjugated —NO_2 group at 7.4 μ and the 9 and 10 μ bands of ferrocene.

The *p*-nitrobenzyl ester was also prepared by treating 3.5 g. (0.0175 mole) of the yellow solid carbonation salt formed from the metalated ferrocenyldiphenylcarbinol with 3.0 g. (0.0175 mole) of *p*-nitrobenzyl chloride in 125 ml. of anhydrous tetrahydrofuran. After 48 hr. reflux, the mixture was treated with water, causing a brown solid to precipitate. This solid was dried and washed several times with ether .After recrystallization from acetone, the orange crystals melted at 246°, in agreement with the previous value. This yield was 3.8 g. (89%).

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The Enol Content of γ-Fluoro-β-keto Esters by Proton Magnetic Resonance

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The enol contents of a number of perfluoroalkyl β-diketones have been determined by Park and co-workers[1] using the Kurt Meyer "indirect" method. In all cases examined, the % enol was over 90% and in fact, several values of 120% were obtained. Other workers[2,3] have reported anomalous values of 115–202% enol for β-diketones in various solvents.

In our studies of fluorine-containing β-keto esters, we were interested in determining the influence of γ-fluorine substitution on the enol content of ethyl acetoacetate (I), which has been shown to possess about 7.5% enol in the pure liquid and 6.9% in methanol at 0°.[4] The marked dependence of the

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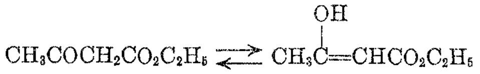
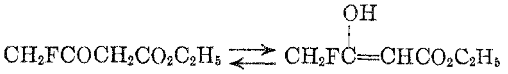
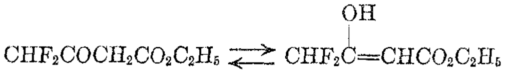
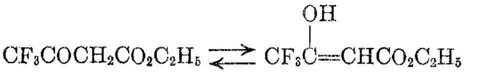
[1] J. D. Park, H. A. Brown, and J. R. Lacher, *J. Am. Chem. Soc.*, **75**, 4753 (1953).

[2] K. Meyer, *Ber.*, **45**, 2843, 2848, 2858 (1912).

[3] J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2952 (1950).

[4] J. B. Conant and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, **54**, 4039 (1932).

TABLE I

Compound	% Enol	
	K. Meyer (CH$_3$OH Solvent)	NMR[9] (Pure Liquid)
 $CH_3COCH_2CO_2C_2H_5 \rightleftharpoons CH_3\overset{\overset{OH}{\vert}}{C}{=}CHCO_2C_2H_5$	6.5	6.0[10]
 $CH_2FCOCH_2CO_2C_2H_5 \rightleftharpoons CH_2F\overset{\overset{OH}{\vert}}{C}{=}CHCO_2C_2H_5$	5.4	7.2 ± 0.2
 $CHF_2COCH_2CO_2C_2H_5 \rightleftharpoons CHF_2\overset{\overset{OH}{\vert}}{C}{=}CHCO_2C_2H_5$	—	53 ± 4
 $CF_3COCH_2CO_2C_2H_5 \rightleftharpoons CF_3\overset{\overset{OH}{\vert}}{C}{=}CHCO_2C_2H_5$	9.9-14.4	89

keto-enol ratio on solvent has been studied in detail.[4]

We therefore attempted to determine the % enol of ethyl 4,4,4,-trifluoroacetoacetate (II) by means of the Meyer technique. In contrast to I, it was observed that the rate of bromine addition to the double bond of the enol form of II was extremely slow, so that the short time interval between the addition of bromine and neutralization of excess bromine was insufficient for reaction with the total amount of enol present in the original sample. The unexpectedly low enol values obtained (10-14%) compared with those reported for the fluorinated β-diketones and the lack of reproducibility of our results, led us to seek a more reliable method for measuring the keto-enol ratio of II.

Since NMR spectra offer a sensitive means for detecting protons in different structural environments, we used this technique[5] to determine quantitatively the per cent enol in I and II, as well as in ethyl 4,4-difluoroacetoacetate[6] and ethyl 4-fluoroacetoacetate.[7] The results are shown in the table.

The spectral analyses were carried out on the pure liquids and were interpreted by comparing half the amplitude of the keto-CH$_2$ peak with the amplitude of the enol $=$CH peak. The NMR method is admirably suited for such determinations for it gives reproducible results, obviates the anomalies and problems mentioned earlier which are associated with the chemical method, and offers the further advantage of small sample requirements. However, this method fails to eliminate true solvent effects, since it is likely that the dielectric constants of the esters differ markedly and the dipole moments of the enol forms may also show considerable differences.[8]

In each of these compounds the enol form is stabilized by hydrogen bonding to the ester carbonyl oxygen atom. It will be noted, however, that the large change in enol content occurs after the introduction of the second fluorine atom. While it would be tempting to propose that O—H - - - -F bonding contributes to further stabilization of the enols, as suggested by Park,[1] the *discontinuity* in the observed per cent enol values disproves this explanation.

One may also postulate that enolization partially relieves the strong electrostatic repulsions between the carbonyl oxygen (of the keto form) and the neighboring fluorine atoms in compound II. However, the —CHF$_2$ and —CH$_2$F groups possess group dipole moments which may point away from the carbonyl oxygen, thus avoiding O—F repulsions. If the variation in enol content were due to this factor, the discontinuity would occur between the —CF$_3$ and —CHF$_2$ analogs, rather than between —CHF$_2$ and —CH$_2$F, as observed.[8]

A consideration worth further examination is that the enols probably become increasingly acidic as the number of fluorine atoms increases. This should lead to increased proton donor capacity and to stronger hydrogen bonding to the ester carbonyl oxygen.

It is also of interest to note that the enol contents of ethyl 4-chloroacetoacetate and ethyl 4,4,4-trichloroacetoacetate have been reported[11] to be 10.9% and 40-50%, respectively (Kurt Meyer). Halogen substitution on the α- position of β-

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(5) We wish to thank Dr. J. N. Shoolery and Mr. Le Roy Johnson of Varian Associates, Palo Alto, Calif., for running and interpreting the NMR spectra of the β-keto esters.

(6) E. T. McBee, O. R. Pierce, H. W. Kilbourne, and E. R. Wilson, *J. Am. Chem. Soc.*, 75, 3152 (1953).

(7) E. D. Bergmann, S. Cohen, and I. Shahak, *J. Chem. Soc.*, 3278 (1959).

(8) We wish to thank the referee for these important observations.

(9) The % enol shown here for ethyl acetoacetate and its trifluoro analog, as measured by NMR, was first reported as No. 43 in a series "This is NMR at Work," Varian Associates Technical Information Bulletin, Vol. 2, No. 2, 1958.

(10) Slightly different values for this compound have been found by the NMR method. Y. Masuda, Kobe University, Japan, private communication, reports 8%; J. D. Roberts, "*Nuclear Magnetic Resonance,*" McGraw-Hill, New York, 1959, p. 68, reports 10%.

(11) F. Arndt, L. Loewe, and L. Capuano, *Rev. faculté sci. univ. Istanbul*, 8A, 122 (1943).

ketoesters lowers the enol/keto ratio. Thus, ethyl α-bromoacetoacetate possesses 4% enol character.[12] It has also been shown[13] that α,γ-difluoroacetoacetate contains 5.2% enol.

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[12] K. H. Meyer, *Ann.*, **380**, 241 (1911).

[13] I. Blank, J. Mager, and E. D. Bergmann, *J. Chem. Soc.*, 2190 (1955).

Methylenecyclopropane *via* Thermal Decomposition of Dimethylaminomethylcyclopropane *N*-Oxide[1,2]

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An earlier paper described the synthesis of bis(dimethylaminomethyl) derivatives of cyclopropane by methylenecyclopropane.[2] Their preparation was of interest as they could possibly serve as precursors for the hydrocarbons dimethylenecyclopropane and trimethylenecyclopropane, provided their deamination could be achieved *via* either the Hofmann elimination method or the thermal decomposition of their *N*-oxides. However, some initial studies in this Laboratory on the deamination of bis(dimethylaminomethyl)cyclopropane, by the above routes, to produce dimethylenecyclopropane, have not been encouraging. It seemed desirable, therefore, to examine carefully the usefulness of deamination procedures in the synthesis of the known simple hydrocarbon methylenecyclopropane (I). Such a study might provide some information pertinent to the optimum experimental conditions for effecting deamination to introduce *exo*-unsaturation in cyclopropane systems.

Demjanow prepared the hydrocarbon I by the Hofmann elimination method[4] and most recently I was obtained in high yield by the decomposition of cyclobutanone tosylhydrazone.[5] Prior to the latter discovery the most convenient route to I was cyclization, by a modified Freund method, of 3-chloro(2-chloromethyl)-1-propene.[6] The most complete account of the properties of I are given in the report by the Ohio State University workers.[6]

For the present study dimethylaminomethylcyclopropane *N*-oxide (II) was obtained smoothly from dimethylaminomethylcyclopropane (III) by the procedure described by Cope.[7] The tertiary amine III was prepared by lithium aluminum hydride reduction of *N,N*-dimethylcyclopropanecarboxamide (IV). Preparation of IV from cyclopropanecarboxylic acid (V)[8] was straightforward.

Thermal decomposition of the *N*-oxide II was effected, over a range of temperature between 135–275°, in a nitrogen atmosphere at 3–5 mm., by slow, dropwise addition of an aqueous sirup of II onto a heated column packed with glass beads. The products formed were trapped as described in the Experimental Section. All olefinic products were initially adsorbed on alumina, then eluted and analyzed by vapor phase chromatography and by determinations of infrared and mass spectra. Three olefins were found as products: the hydrocarbon I together with isobutylene and 1,3-butadiene. Decomposition of the *N*-oxide II to the tertiary amine III was not observed. The three stated olefins were produced in low conversion and in yields which varied from *ca.* 4–12% with changes in pyrolysis temperatures. At best, the hydrocarbon I was obtained in *ca.* 6.5% yield at 210°. At this temperature, the optimum one for obtaining I, isobutylene and 1,3-butadiene were each produced in *ca.* 3% yield.[9] It was shown by an independent experiment that authentic I did not give either isobutylene or 1,3-butadiene under the pyrolysis conditions.

In conclusion it should be pointed out that the thermal decomposition of the amine oxide II contrasts sharply with similar decompositions of amine oxide derivatives of higher ring systems, *i.e.*, those with four through seven ring members.[10,11,12] In these systems amine oxide decompositions generally give 60–80% yield of olefin product.

EXPERIMENTAL

Materials. 1,3-Butadiene and isobutylene, obtained from The Matheson Co., were C.P. grade. Methylenecyclopropane, prepared as described earlier,[6] was found by vapor phase chromatography (VPC) analysis to contain 14% isobutylene.

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[1] This is the twelfth publication concerned with the chemistry of small carbon rings. For the preceding paper, see A. T. Blomquist and E. A. LaLancette, *J. Am. Chem. Soc.*, **83**, 1387 (1961).

[2] For a closely related paper see A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **81**, 2012 (1959).

[3] Supported by funds received from a Du Pont Grant-in-Aid, Summer, 1959; Dow Chemical Co. Fellow, Summer, 1960.

[4] N. J. Demjanow and M. Dojarenko, *Ber.*, **56**, 2208 (1923).

[5] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

[6] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953).

[7] A. C. Cope, N. A. LeBel, H.-H. Lee, and W. R. Moore, *J. Am. Chem. Soc.*, **79**, 4720 (1957).

[8] C. M. McCloskey and G. H. Coleman, *Org. Syntheses*, **Coll. Vol. III**, 221 (1958).

[9] Under the pyrolysis conditions described *N,N*-dimethylbutylamine *N*-oxide gave consistently 90–95% pure 1-butene.

[10] H. E. Baumgarten, F. A. Bower, and T. T. Okamoto, *J. Am. Chem. Soc.*, **79**, 3145 (1957).

[11] A. C. Cope, C. L. Bumgardner, and E. F. Schweizer, *J. Am. Chem. Soc.*, **79**, 4729 (1957).