on photolysis of benzene solutions of the two diazo esters in Pyrex vessels. Cuprous bromide catalyzed decomposition of diethyl diazomalonate in benzene occurred at 80° and gave tetraethyl ethylenetetracarboxylate in 40% yield.

Experimental Section

Diethyl Mesoxalate Hydrazone.—The procedure of Staudinger and Hammett[7] was modified slightly. To a cooled mixture of 50 ml. of water and 50 ml. (52 g., 0.87 mole) of acetic acid was added slowly 30 g. (0.6 mole) of hydrazine hydrate; the temperature was kept below 25°. Diethyl mesoxalate (52 g., 0.3 mole, Columbia Chemical Co.) was then added slowly, keeping the temperature below 20°. After standing at room temperature for 18 hr., the crystals were collected and washed well with water. Drying over sodium hydroxide–silica gel gave 39.1 g. of diethyl mesoxalate hydrazone, m.p. 77–80° (lit.[7] m.p. 80°). A second crop of 3.1 g. of the hydrazone, m.p. 77–78°, crystallized from the mother liquor on standing for 2 days. The total yield was 42.2 g. (75%). The ultraviolet spectrum of diethyl mesoxalate hydrazone (in acetonitrile) showed a maximum at 270 mμ (ϵ 9500); the infrared showed $\nu_{\max}^{\mathrm{KBr}}$ 3320 (s), 3180 (s), 2990 (m), 2940 (w), 2910 (w), 1695 (s), 1680 (s), and 1585 cm.$^{-1}$ (s), among others. The n.m.r. showed (30% in perdeuterioacetone) showed a broad singlet at τ 0.46 (half-band width 12 c.p.s., two protons), two sets of quartets centered at τ 6.2 (separation between the two sets of components was 3.2 c.p.s., four protons), and two sets of triplets at τ 9.2 (separation between the two sets of components was 1.2 c.p.s., six protons).

Diethyl Diazomalonate.—A mixture of 20.0 g. (0.106 mole) of diethyl mesoxalate hydrazone, 100 g. (0.43 mole) of silver oxide,[10] 45 g. of magnesium sulfate, and 300 ml. of tetrahydrofuran was stirred vigorously (mechanical stirrer) at room temperature for 4 hr. The mixture was filtered, the solids were washed with tetrahydrofuran, and the combined filtrate and washings were concentrated, using a rotary evaporator. Distillation of the residue gave 17.62 g. (89%) of diethyl diazomalonate: b.p. 58° (0.3 mm.); m.p. 9°; $n^{24}\mathrm{D}$ 1.4650 (lit.[4] b.p. 84–85° at 1 mm., m.p. 7–8° $n^{25}\mathrm{D}$ 1.4630); $\lambda_{\max}^{\mathrm{cyclohexane}}$ 352 mμ (ϵ 23) and 252 mμ (ϵ 7400); $\nu_{\max}$ (pure liquid, values in 20% CCl_4 in parentheses) 2150 (2130), 1765 (1760), 1740 (1735), and 1695 (1685) cm.$^{-1}$, among others; n.m.r. spectrum (10% in CCl_4), triplet centered at τ 8.67 (six protons) and quartet centered at τ 5.72 (four protons); dipole moment 2.66 D. (at 25° in dioxane).

Anal. Calcd. for $C_7H_{10}N_2O_4$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.47; H, 5.44; N, 15.09.

Dimethyl Mesoxalate Hydrazone.—A saturated (at room temperature) solution of dry gaseous hydrogen chloride in 1300 ml. of anhydrous methanol was cooled to 5°, and a solution of 200 g. of diethyl mesoxalate hydrazone in 1300 ml. of methanol was added. The mixture stood at ice-bath temperature for 2 hr. and then at room temperature overnight. Some gas evolution occurred. The mixture was concentrated to dryness at room temperature using a rotary evaporator with a trap cooled with Dry Ice–acetone. The residue was dried over potassium hydroxide, washed with one 200-ml. and two 100-ml. portions of water, and dried again, giving 69 g. of a pale yellow semisolid. Crystallization from 70 ml. of acetonitrile gave 43.3 g. (25% yield) of dimethyl mesoxalate hydrazone, m.p. 132.5–134°. An analytical sample, prepared by recrystallization from acetonitrile, had m.p. 134–135°; $\lambda_{\max}^{\mathrm{EtOH}}$ 283 mμ (ϵ 9900), $\lambda_{\max}^{\mathrm{MeCN}}$ 272 mμ (ϵ 9400); $\nu_{\max}^{\mathrm{KBr}}$ 3300 (s), 3170 (s), 3030 (w), 2960 (w–m), 1700 (vs), 1680 (s), and 1585 cm.$^{-1}$ (s), among others; n.m.r. spectrum (in $CDCl_3$), broad band at τ 0.42 (half-band width 14 c.p.s., two protons) and two singlets at τ 6.1, separation 1.4 c.p.s. (three protons each).

Dimethyl Diazomalonate.—Dimethyl mesoxalate hydrazone (45 g.) was oxidized with 220 g. of silver oxide in 600 ml. of tetrahydrofuran as described for the preparation of diethyl diazomalonate. Distillation gave 39.35 g. (89% yield) of dimethyl diazomalonate: b.p. 45° (0.2 mm.) (lit.[3] b.p. 63° at 1 mm.); $n^{25}\mathrm{D}$ 1.4808; $\lambda_{\max}^{\mathrm{cyclohexane}}$ 352 mμ (ϵ 22), 250 mμ (ϵ 7900), and 225 mμ (sh) (ϵ 7300); $\nu_{\max}^{\mathrm{neat}}$ 3020 (m), 2960 (s), 2850 (w), 2150 (s), 1770 (s), 1745 (s), and 1680 cm.$^{-1}$ (s), among others; n.m.r. spectrum (in $CDCl_3$), singlet at τ 6.24.

Dimethyl Mesoxalate Triphenylphosphazine.—A solution of 1.147 g. of dimethyl diazomalonate and 2.01 g. of triphenylphosphine in 8 ml. of ether stood at room temperature overnight. The yellow crystals were collected, washed with ether, and dried, giving 2.498 g. (82% yield) of dimethyl mesoxalate triphenylphosphazine, m.p. 93–95° (lit.[11] m.p. 93°).

Anal. Calcd. for $C_{23}H_{21}N_2O_4P$: C, 65.71; H, 5.04; N, 6.66; P, 7.37. Found: C, 65.87; H, 5.26; N, 6.51; P, 7.12.

Reaction of Dimethyl Mesoxalate with Hydrazine.—To a mixture of 63 ml. of acetic acid and 63 ml. of water was added slowly with stirring and cooling 34.2 g. (0.64 mole) of hydrazine hydrate, followed by 50.0 g. (0.34 mole) of dimethyl mesoxalate.[12] A white precipitate formed almost immediately. It was collected by filtration, washed with water and dried, giving 44.83 g. (81%) of crude 1,2-bis[hydroxybis(methoxycarbonyl)methyl]-hydrazine, m.p. 161° dec. An analytical sample, prepared by recrystallization from acetonitrile, had m.p. 163° dec. (lit.[9] m.p. 154–155°); n.m.r. spectrum (in perdeuteriodimethyl sulfoxide), singlets at τ 3.1 (two protons), 5.3 (two protons), and 6.3 (six protons); $\nu_{\max}^{\mathrm{KBr}}$ 3420 (s), 3270 (m), 2970 (m), and 1755 (s) cm.$^{-1}$, among others.

The filtrate, on standing for 3 days, deposited 2.46 g. (5% yield) of dimethyl mesoxalate hydrazone in the form of colorless crystals.

Thermolysis of Diethyl Diazomalonate in the Presence of Cuprous Bromide.—A mixture of 289 mg. of diethyl diazomalonate, 284 mg. of cuprous bromide, and 4 ml. of benzene was heated under reflux for 8 hr. during which time 0.92 mole of nitrogen was evolved. Removal of the solvent from the filtered solution gave 268 mg. of a yellow oil which was seeded with a small crystal of tetraethyl ethylenetetracarboxylate. The resulting semisolid was pressed on a porous plate, giving 90 mg. (40% yield) of tetraethyl ethylenetetracarboxylate, m.p. 51–53° (lit.[13] m.p. 52.5–53.5°), the infrared spectrum of which was identical with that of an authentic sample.[13]

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[10] Best results were obtained with silver oxide that had been freshly precipitated, washed well with water, and dried.

[11] H. Staudinger and P. Lüscher, *Helv. Chim. Acta*, **5**, 75 (1922).

[12] Dimethyl mesoxalate, b.p. 106–109° (40 mm.), $n^{25}\mathrm{D}$ 1.4172, was preprepared according to A. W. Dox, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 266, using commercial nitrogen dioxide.

[13] B. B. Corson and W. L. Benson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 273.

Addition of Oxygen Difluoride to Tetramethylallene[1]

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Oxygen difluoride (OF_2) has been shown[2] to add smoothly to various aliphatic olefins under stringently controlled conditions. Extension of this low-temperature (−78°) technique to acetylenes[2] was successful and the postulated intermediates were vinyl hypofluorites. It should then be expected that the primary OF_2 addition product of an allene would be a similar hypofluorite which would rearrange[2] to an α,α'-difluoro ketone.

Tetramethylallene consumed 1 equiv. of OF_2 at −78° to produce two volatile products assigned the structures 2,4-difluoro,2,4-dimethylpentanone-3 (I) and 2-fluoro-2,4-dimethylpent-4-en-3-one (II).

The structures of compounds I and II are based on infrared, proton, and F^{19} n.m.r. spectra. The spontaneous decomposition and loss of HF unfortunately

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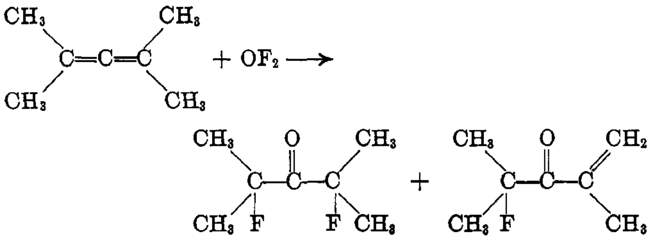
[1] This work was sponsored under Army Ordnance Contract No. DA-01-021 ORD-11878.

[2] R. F. Merritt and J. K. Ruff, *J. Org. Chem.*, **30**, 328 (1965).



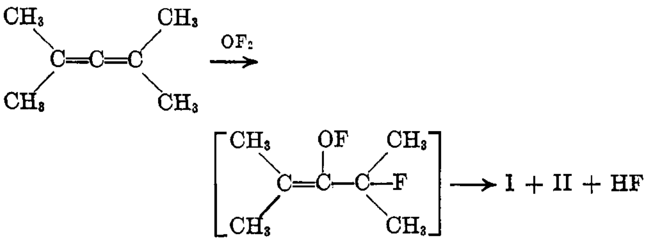
I II

precluded elemental analysis. The infrared spectrum of compound I contained a carbonyl group absorption at 1730 cm.$^{-1}$ representing a shift in the proper direction caused by the fluorine atoms on the α position.[3] The proton n.m.r. spectrum consisted of a doublet (J_{HF} = 20 c.p.s.) centered at δ 1.52. The proton–fluorine coupling is normal[4] for vicinal coupling. Geminal H–F^{19} coupling constants are usually in the order of 40–80 c.p.s.[4] The four methyl groups appear as a single doublet which is indicative of symmetrical substitution as well as the fact that the methyl protons are vicinal to a single fluorine atom. The F^{19} n.m.r. spectrum exhibited a septet structure centered at ϕ +148.3[5] (J_{FH} = 20 c.p.s.) which is typical of a fluorine atom coupling with six equivalent vicinal protons.

The α,β unsaturation of ketone II caused the carbonyl absorption to shift to 1681 cm.$^{-1}$ as expected[3] for this class of compound. The proton n.m.r. spectrum is consistent with the structure II in that the fluoroisopropyl group is a six-proton doublet (J_{FH} = 20 c.p.s.) centered at δ 1.52. The vinylogous protons (two) appear as the characteristic set of multiplets at δ 5.82 and 6.23. The remaining 3-proton broadened singlet at δ 1.90 is assigned to the vinylogous methyl group. The F^{19} n.m.r. spectrum consists of a septet (J_{FH} = 20 c.p.s.) centered at ϕ +144.6 which is again consistent with a single fluorine atom coupling with six equivalent vicinal protons.

The exact character of the attacking species cannot be inferred unequivocally from the existing data. It is very possible that an α-fluorovinyl hypofluorite (III), similar in nature to those postulated in acetylene–OF_2 additions, is first formed, which subsequently isomerizes with fluorine migration to the observed α,α'-difluoro ketone. The migration step includes the probable homolytic fission of the O–F bond followed by either C–F bond formation forming compound I or HF elimination leading to ketone II.

The addition of OF_2 to tetrafluoroallene has been recently reported.[6] The products are not revealing mechanistically, but a low yield of a three-carbon unsaturated hypofluorite of undefined structure was actually isolated. Hypofluorites containing, or in the presence of, C–H bonds have been shown by Thompson and Prager[7] to be of very limited stability and hence would not be expected to survive intact in the tetramethylallene case.



III

Experimental Section

Tetramethylallene (2.4 g., 25 mmoles) was dissolved in 20 ml. of CCl_3F and this mixture was slurried with 1.0 g. of NaF. The slurry was stirred vigorously and degassed at −78°; the OF_2 (25 mmoles) was slowly admitted to the reaction vessel with care to ensure that the pressure of OF_2 never exceeded 20 mm. When the uptake was complete, the volatile products were distilled under reduced pressure from the reactor. The solvent was separated and the residue (~2.1 g.) was rectified by vapor phase chromatography (GESF96 at 68°). Decomposition of both components started when the crude mixture was warmed to ambient temperature and continued throughout the purification procedure. Owing to the instability of the compounds, no estimate of the yield could be made.

Acknowledgment.—The author is grateful to Mr. Jack Brooks for technical assistance and to Mrs. Carolyn Haney for the n.m.r. spectra.

[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[4] J. A. Pople, *Mol. Phys.*, 1, 216 (1958).

[5] Fluorine n.m.r. spectra are reported in ϕ values (parts per million from internal CCl_3F).

[6] R. Reed, Jr., K. Prabil, and L. Marantz, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[7] P. G. Thompson and J. H. Prager, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

Isomerization of Alkyl Tropilidenes. II. Rearrangement during Gas Chromatography

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Two mechanisms have been shown to be responsible for the isomerization of samples of 7-methyltropilidene subjected to gas chromatography on certain columns: an acid-catalyzed mechanism and an intermolecular hydride-exchange mechanism. The most striking evidence for the latter mechanism is that a sample of 7-methyltropilidene injected on a tropylium fluoborate–nitromethylpimelonitrile column results in the elution of tropilidene exclusively.

Our interest in this isomerization during gas chromatography (g.c.) arose when, during a search for a column for g.c. analysis of the isomers of methyltropilidene,[2] very unusual behavior was noted when a picric acid–fluorene column[3] was used. Pure 7-methyltropilidene gave rise to a very broad peak, and rechromatography of the collected eluate on a suitable column revealed that isomerization of the 7 isomer to a mixture of the 1-, 2-, 3-, and 7-methyltropilidenes had occurred.

At least three different mechanisms can be postulated by which this isomerization might be explained: (1) thermally induced intramolecular hydride transfer in the tropilidene[4]; (2) protonation to form a cyclo-

[1] Undergraduate Science Education Fellow of the National Science Foundation, 1962–1963.

[2] K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).

[3] A. I. M. Keulemans, A. Kwantes, and P. Zaal, *Anal. Chim. Acta*, **13**, 357 (1955).

[4] A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962).