acid plus 50 ml. of concentrated hydrochloric acid. Warming the reaction mixture under reduced pressure removed some of the solvent and any bromine that remained. The mixture, diluted by the slow addition of water, was allowed to stand in the refrigerator for 1 day. The dried, off-white, crystalline precipitate (II) weighed 12 g. and melted at 80–84°. Two crystallizations from aqueous methanol gave pure N-(3-bromo-2-chloropropyl)benzenesulfonamide (II), m.p. 82–83.5°.

Anal. Calcd. for $C_9H_{11}BrClNO_2S$: C, 34.57; H, 3.55; N, 4.48. Found: C, 34.56; H, 3.65; N, 4.48.

1-Benzenesulfonyl-2-bromomethylenimine (I) from N-(3-Bromo-2-chloropropyl)benzenesulfonamide (II).—Although compound II dissolved in 5% aqueous sodium hydroxide, the solution soon became cloudy and deposited a crystalline precipitate. After 2 hr., the mixture was filtered, and the solid was washed with water and dried *in vacuo* over calcium chloride. This material, 1-benzenesulfonyl-2-bromomethylethylenimine (I), melted sharply without further purification at 84.5–85.5°. When mixed with authentic material, m.p. 86–88°, the cyclized product showed m.p. 85–86.5°. Comparison of infrared spectra confirmed the identity of the cyclized material as 1-benzenesulfonyl-2-bromomethylethylenimine (I) but also indicated the presence of trace amounts of impurities.

1-Bromo-2-benzenesulfonamido-3-chloropropane (III) from 1-Benzenesulfonyl-2-bromomethylethylenimine (I) and Hydrochloric Acid.—A mixture of 2.0 g. (7.2 mmoles) of 1-benzenesulfonyl-2-bromomethylethylenimine (I) and 22 ml. of 37% hydrochloric acid was stirred and heated on the steam bath under a condenser for 3.5 hr. After addition of 62 ml. of water, the reaction mixture was cooled in ice. The collected precipitate, dissolved in methanol, was first filtered through decolorizing carbon and then crystallized twice from aqueous methanol. The pure white, crystalline 1-bromo-2-benzenesulfonamido-3-chloropropane (III), m.p. 85.5–87°, weighed 1.7 g. (68%). Two additional crystallizations did not change the melting point.

Anal. Calcd. for $C_9H_{11}BrClNO_2S$: C, 34.58; H, 3.45; N, 4.48. Found: C, 34.34; H, 3.45; N, 4.41.

A mixture of product III with the starting material I melted at 65–85°.

1-Benzenesulfonyl-2-chloromethylethylenimine (V) from 1-Bromo-2-benzenesulfonamido-3-chloropropane (III).—A solution of 1.0 g. (3.2 mmoles) of 1-bromo-2-benzenesulfonamido-3-chloropropane in 10 ml. of 95% ethanol containing 50 ml. of 0.094 *N* aqueous sodium hydroxide was diluted with 25 ml. of water and was allowed to stand at 0°. The crystalline precipitate, obtained in near quantitative yield, was crystallized from aqueous methanol to give 0.75 g. (85%) of 1-benzenesulfonyl-2-chloromethylethylenimine (V), m.p. 83.5–84.5°. The melting point was not changed by two additional crystallizations. A mixture melting point with starting material II, m.p. 85.5–87°, was depressed to 70–85°.

Anal. Calcd. for $C_9H_{10}ClNO_2S$: C, 46.64; H, 4.34; Cl, 15.30; N, 6.05. Found: C, 46.65; H, 4.29; Cl, 15.27; N, 6.07.

A Convenient Synthesis of Dimethyl and Diethyl Diazomalonate

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Contribution No. 1122 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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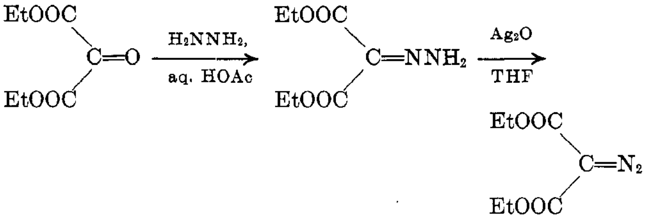
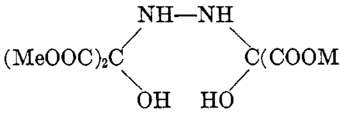
The finding[1] that two cyano groups in the 7-position stabilize the norcaradiene skeleton led us to investigate the effect of other electron-withdrawing groups on the position of the norcaradiene–cycloheptatriene equilibrium.[2] To that purpose we attempted to prepare the adducts of benzene to dialkoxycarbonylcarbenes, generated by thermolysis of photolysis of the corresponding dialkyl diazomalonates. Although these attempts were abortive because of the failure of the carbenes to add to benzene, we wish to report here convenient syntheses for two precursors, dimethyl and diethyl diazomalonate.

Diethyl diazomalonate has been prepared by diazotization of diethyl aminomalonate,[3] but the product obtained by this method is grossly contaminated by ethyl diazoacetate[4] and has to be purified by repeated distillation and recrystallization. Similarly, diethyl diazomalonate obtained[5] by the reaction of ethyl diazoacetate with phosgene followed by addition of ethanol is contaminated by chlorine-containing by-products.[6] We have found that the diazo ester may be prepared in 67% over-all yield and in a high state of purity from commercially available diethyl mesoxalate. Treatment of the latter in aqueous acetic acid solution with hydrazine gave diethyl mesoxalate hydrazone in 75% yield. Oxidation of the hydrazone with silver oxide in tetrahydrofuran produced gas chromatographically pure diethyl diazomalonate in 89% yield. Diethyl mesoxalate hydrazone has been described previously,[7] and the fact that it is readily oxidized to diethyl diazomalonate has also been mentioned.[8] When dimethyl mesoxalate was treated with hydrazine under the conditions described for the diethyl analog, mainly the hydrazine derivative 1[9] and only a small amount of the desired dimethyl mesoxalate hydrazone were obtained. Since dimethyl mesoxalate is not commercially available, this approach was abandoned in favor of one involving transesterification of diethyl mesoxalate hydrazone with methanol and hydrochloric acid. Yields of dimethyl mesoxalate hydrazone were only moderate (25%), but the procedure could be scaled up to a molar scale without any difficulties. Oxidation of the hydrazone with silver oxide in tetrahydrofuran furnished dimethyl diazomalonate in 89% yield.





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Complete thermolysis of diethyl and dimethyl diazomalonate in benzene required a temperature of 150°. The products were complex mixtures, the analyses and molecular weight determinations of which indicated that they were mostly dimers of the dialkoxycarbonylcarbenes. Similar mixtures were obtained

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[1] E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965).

[2] E. Ciganek, *ibid.*, **87**, 1149 (1965).

[3] H. Lindemann, A. Wolter, and R. Groger, *Ber.*, **63**, 702 (1930).

[4] W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

[5] H. Staudinger, J. Becker, and H. Hirzel, *Ber.*, **49**, 1978 (1916).

[6] See ref. 5, footnote 1 on p. 1984.

[7] H. Staudinger and L. Hammett, *Helv. Chim. Acta*, **4**, 217 (1921).

[8] J. Neresheimer, Doctoral Dissertation, Munich, 1908.

[9] R. S. Curtiss and P. T. Tarnowski, *J. Am. Chem. Soc.*, **30**, 1264 (1908).

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 ν_{max}^{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°; $n^{24}\text{D}$ 1.4650 (lit.[4] b.p. 84–85° at 1 mm., m.p. 7–8° $n^{25}\text{D}$ 1.4630); $\lambda_{max}^{cyclohexane}$ 352 mμ (ϵ 23) and 252 mμ (ϵ 7400); ν_{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°; λ_{max}^{EtOH} 283 mμ (ϵ 9900), λ_{max}^{MeCN} 272 mμ (ϵ 9400); ν_{max}^{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.); $n^{25}\text{D}$ 1.4808; $\lambda_{max}^{cyclohexane}$ 352 mμ (ϵ 22), 250 mμ (ϵ 7900), and 225 mμ (sh) (ϵ 7300); ν_{max}^{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); ν_{max}^{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.), $n^{25}\text{D}$ 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).