TABLE I

	Yield, %	Active bromine, % of theory	Mp, °C Obsd (crude)	Mp, °C Lit.
N-Bromo derivative of				
succinimide	98	95	168–169 dec	178 dec[a]
phthalimide	99	95	201–203 dec	206–207 dec[b]
N-methyl-4-nitrobenzamide	99	99	113–115 dec	
N-*t*-butyl-4-nitrobenzamide	99	97	131–134 dec	
4-nitrobenzamide	99	95	229–231 dec	192–202[c]
trifluoroacetamide	85	99	52–54 dec	62[d]
benzamide	98	94	126–128 dec	129–131dec[c]
N-methyl-4-toluenesulfonamide	101	98	106–107 dec	113 dec[a]
N,N-Dibromo derivative of				
4-nitrobenzamide	99	100	138–139 dec	
4-toluenesulfonamide	101	99	95–97 dec	104[a]

[a] Reference 1a. [b] Reference 4. [c] Reference b. [d] Reference 2.

the active-bromine compound in acetone, adding an equal volume of a 50:50 mixture of acetic acid and water plus an excess of potassium iodide and titrating for the released iodine with standard thiosulfate solution.

Acetyl Hypobromite.[5]—A mixture of silver acetate (5.6 g, 0.033 mol) and 150 ml of carbon tetrachloride was placed in a 500-ml round-bottom flask covered with aluminum foil. To the stirred mixture a carbon tetrachloride solution of bromine (2.15 *M*, 0.032 mol) was added dropwise over a period of 10 min as the reaction temperature was maintained at −10 ± 5°. The mixture was stirred for an additional 10 min and then filtered. The carbon tetrachloride solution was diluted to 200 ml (0.136 *M*, 0.027 mol). All other acetyl hypobromite solutions were prepared in a similar manner. Solutions of acetyl hypobromite were stable up to four weeks when stored in the dark at −10 to −15° temps. Solutions that were exposed to ordinary light at room temperature showed no activity after 8 hr. No problems were observed owing to rapid decomposition of the acetyl hypobromite.

N-Bromo-N-*t*-butyl-4-nitrobenzamide.—A mixture of N-*t*-butyl-4-nitrobenzamide (0.119 g, 0.5360 mmol) and 8 ml of acetyl hypobromite solution (0.108 *M*, 0.8061 mmol) in carbon tetrachloride was stirred at ambient temperature for 15 min in a 25-ml round-bottom flask. The flask was covered with aluminum foil to protect the product from light. The solution was evaporated at reduced pressure giving 0.1586 g of product, mp 136–137° (99% yield, active bromine was 97% of theory).

The product was recrystallized from an acetone–water mixture, giving an analytically pure material, mp 137–138° dec, ir 6.06 μ (Nujol mull) with no NH peak, uv 268 mμ (dioxane).

Anal. Calcd for $C_{11}H_{13}N_2O_3Br$: Br, 26.53. Found: Br, 26.34.

N,N-Dibromo-4-nitrobenzamide.—A mixture of 4-nitrobenzamide (0.173 g, 1.038 mmol) and 20 ml of acetyl hypobromite (0.124 M, 2.48 mmol) in carbon tetrachloride was stirred at ambient temperature for 75 min in a 50-ml round-bottom flask. The flask was covered with aluminum foil. The solution was evaporated at reduced pressure giving 0.332 g of analytically pure material, mp 138–139° dec (99% yield, active bromine was 99.7% of theory), ir 5.97 μ (Nujol mull) with no NH peak, uv 291 mμ (dioxane).

Anal. Calcd for $C_7H_4N_2O_3Br_2$: Br, 49.33. Found: Br, 49.18.

N-Bromobenzamide.—A mixture of benzamide (0.145 g, 1.20 mmol and 10 ml of acetyl hypobromite (0.126 M, 1.26 mmol) was stirred in the dark in a 25-ml round-bottom flask for 60 min at ambient temperatures. The mixture was evaporated at reduced pressure leaving 0.235 g of product, mp 126—128° dec (lit.[6] mp 129–131° dec) (98% yield, active bromine was 95% of theory).

N-Bromo-N-methyl-4-nitrobenzamide.—The N-methyl-4-nitrobenzamide was N-brominated in manner previously described in the N-*t*-butylamide. The N-bromo product was recrystallized from an acetone–water mixture, giving analytically pure material, mp 114–115° dec, ir 6.05 μ (Nujol mull) with no NH peak, uv 268 mμ (dioxane).

Anal. Calcd for $C_8H_7N_2O_3Br$: Br, 30.84. Found: Br, 30.53.

N-Iodosuccinimide.—A mixture of succinimide (0.166 g, 1.67 mmol), silver acetate (0.646 g, 3.87 mmol), and 10 ml of acetone was placed in a 50-ml round-bottom flask covered with aluminum foil. The flask was cooled in an ice bath and a solution of iodine (0.468 g, 1.84 mmol) in 15 ml of acetone was dropped in over a 5-min period. Stirring was continued for an additional 10 min. The mixture was filtered; the acetone solution was evaporated leaving 0.353 g (94% yield, active iodine was 96% of theory) of material, mp 191–193° dec (lit.[7] mp 201° dec).

Registry No.—Acetyl hypobromite, 4254-22-2; N-bromo-N-*t*-butyl-4-nitrobenzamide, 24472-09-1; N,N-dibromo-4-nitrobenzamide, 24472-10-4; N-bromo-N-methyl-4-nitrobenzamide, 24472-11-5.

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A Convenient Procedure for the Methylenation of Olefins to Cyclopropanes

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The methylenation of olefins by the method of Simmons and Smith,[2] utilizing methylene diiodide and zinc–copper couple, provides a most convenient and much used entry into the cyclopropane field. However, in spite of various modifications,[3,4] the experimental procedure still requires the preparation of rather irreproducible zinc–copper reagents.

We find that a separate preparation of the zinc–copper couple is not required; a mixture of zinc dust and a cuprous halide is even more effective. This modification reduces the experimental difficulties to the level of those encountered in an ordinary Grignard reaction.

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The experimental procedure is illustrated by the methylenation of cyclohexene. A mixture of zinc dust (17.0 g, 0.26 mol) and cuprous chloride (2.58 g, 0.26 mol) in 40 ml of ether was stirred and heated to reflux in a nitrogen atmosphere for 30 min. Cyclohexene (10.1 ml, 0.1 mol) was then added, followed by methylene diiodide (10.5 ml, 0.13 mol) and the mixture was maintained at reflux for 24 hr. A 92% yield (gas chromatography) of bicyclo[4,1,0]heptane was obtained. The following olefins were also methylenated: cyclooctene (94%), cyclododecene (79%), and styrene (69%). The cuprous halide could be replaced by copper powder, although yields were slightly lower (87% from cyclohexene). In an alternative procedure the reagent was preformed from the cuprous chloride, zinc dust, and methylene diiodide and refluxed for a further 30 min before addition of the olefin.

Registry No.—Zinc, 7440-66-6; cuprous chloride, 7758-89-6.

Cycloaddition Reactions of Cyclopropanones[1]

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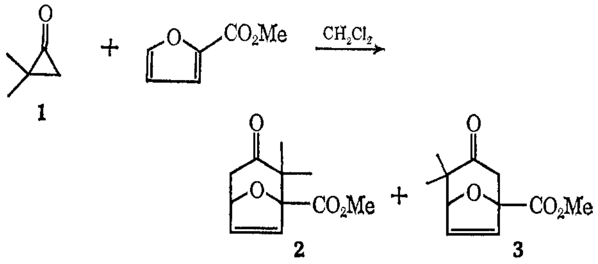
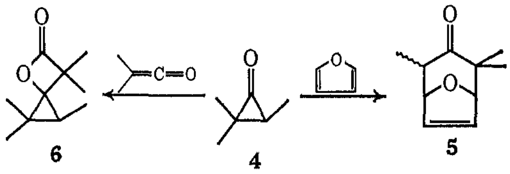
Cyclopropanones have been shown to undergo 2 + 2 → 4, 3 + 2 → 5, and 3 + 4 → 7 cycloaddition reactions.[5-14] In addition, similar 3 + 4 → 7 adducts have been reported in several studies of supposed Favorskii intermediates.[15-17] We wish to report several new examples of these cycloadducts.

2,2-Dimethylcyclopropanone (**1**) reacts with 2-carbomethoxyfuran to form adducts **2** and **3** in the ratio of *ca.* 7.5:1 in greater than 70% yield (eq 1). 2,2,3-Trimethylcyclopropanone (**4**) reacts with furan to form adduct **5** in over 90% yield and with dimethylketene to form adduct **6** as the only product (eq 2).

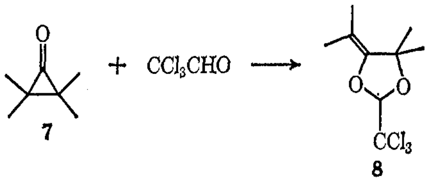


(1)



(2)

Tetramethylcyclopropanone (**7**) reacts with chloral to form adduct **8** as the only product (eq 3).



(3)

These adducts were characterized unambiguously on the basis of spectral data (see Experimental Section). Their spectral characteristics correlate very well with previously reported adducts.[8]

The results reported here, when combined with previous work on the cycloaddition of cyclopropanones,[9-14] clearly demonstrate the generality and synthetic value of these reactions.

Experimental Section

1-Carbomethoxy-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (2) and 1-Carbomethoxy-4,4-dimethyl-8-oxabicyclo[3.2.1]-oct-6-en-3-one (3).—2-Carbomethoxyfuran (2 ml, 18.7 mmol) was mixed with a CH$_2$Cl$_2$ solution (7 ml) of 2,2-dimethylcyclopropanone (13.3 mmol), and the mixture was left at room temperature for several days. Removal of the solvent on a "Roto-Vap" followed by preparative vpc (6 ft × $^3/_8$ in., 20% SE-30, Chromosorb P, 200 ml of He/min, 198°) resulted in the isolation of a mixture of **2** and **3**. Adduct **2** was the major isomer by ≈7.5 to 1. Attempts to separate the two isomers by vpc (*βββ*, Carbowax, diisodecyl phthalate) or by tlc (silica or alumina) were unsuccessful. Adduct **2** had the following nmr spectrum (CCl$_4$–TMS): δ 1.07 (s, 3 H), 1.17 (s, 3 H), 2.50 (AB, 2 H, $J_{AB} = 17$ Hz, $\Delta\nu_{AB} = 39.4$ Hz, low field half split further $J = 5$ Hz, high field half split further $J = 1.5$ Hz), 3.77 (s, 3 H), 4.99 (d of t, 1 H, $J = 5$ and 1.5 Hz), 6.32 (AB, 2 H, $J_{AB} = 6$ Hz, $\Delta\nu_{AB} = 5.9$ Hz, high field half split further $J = 1.5$ Hz). Adduct **3** had the following nmr spectrum (CCl$_4$–TMS): δ 0.94 (s, 3 H), 1.28 (s, 3 H), 2.60 (AB, 2 H, $J_{AB} = 16.5$ Hz, $\Delta\nu_{AB} = 22.7$ Hz), 3.77 (s, 3 H), 4.48 (d, 1 H, $J = 1.5$ Hz), 6.32. (The olefinic and methoxyl protons of **3** could not be distinguished from those of **2**.) In a previous small-scale reaction, the yield of adducts had been greater than 70% (nmr). Mass spectra of **2** and **3** (75 ev): *m/e* (rel intensity) 210 (M$^+$, 46), 178 (73), 153 (10), 150 (6), 140 (100), 134 (9), 125 (41), 109 (59), 108 (64), 95 (21), 81 (75), 79 (10), 70 (72), 69 (12), 53 (27), 44 (34), 43 (25), 42 (28), 41 (31), 40 (37), 39 (20).

2,2,4-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (5).—A dilute (2–3%) CH$_2$Cl$_2$ solution of **4**[18] (15 ml) was mixed with 5 ml of purified furan (∼69 mmol). After 1 hr at room temperature, evaporation of the solvent followed by preparative vpc (6 ft. × $^3/_8$ in., 22% Carbowax 20M, Chromosorb P, 200°, 120 cc of He/min) led to the isolation of adduct **5** which was identified by the following spectral properties: ir ν_{max}^{neat} 1715 (C═O), 1380

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