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]

N. J. Turro,[2] S. S. Edelson,[3] and R. B. Gagosian[4]

Department of Chemistry, Columbia University, New York, New York 10027

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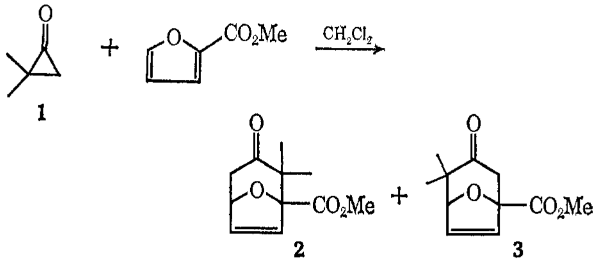
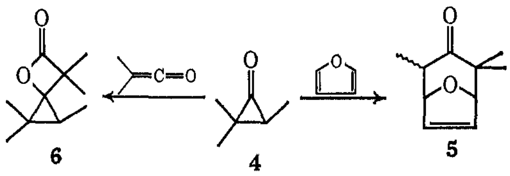
Cyclopropanones have been shown to undergo 2 + 2 → 4, 3 + 2 → 5, and 3 + 4 → 7 cycloaddition reactions.[5–14] In addition, similar 3 + 4 → 7 adducts have been reported in several studies of supposed Favorskii intermediates.[15–17] We wish to report several new examples of these cycloadducts.

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).

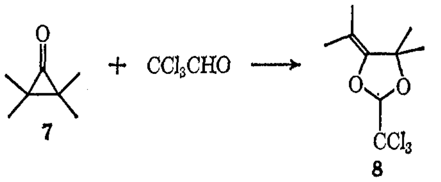


(1)



(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_2Cl_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 (*ββ′β*, 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 = 1.5 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_2Cl_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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[1] (a) Cyclopropanones. XVIII. Paper XVII: S. S. Edelson and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2770 (1970). (b) The authors wish to thank the U. S. Air Force Office of Scientific Research for their generous support of this work (Grants AFOSR-66-1000 and AFOSR-68-1381). A gift from the Upjohn Co. is also gratefully acknowledged.

[2] Alfred P. Sloan Fellow, 1966–1970.

[3] National Science Foundation Trainee, 1965–1966; National Science Foundation Predoctoral Fellow, 1966–1969.

[4] National Science Foundation Trainee, 1967–1968; Ferguson Teaching Fellow, 1968–1969.

[5] R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc. London*, 144 (1964).

[6] H. G. Richey, J. M. Richey, and D. C. Clagett, *J. Amer. Chem. Soc.*, **86**, 3906 (1964).

[7] N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2774 (1965).

[8] See N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *ibid.*, **91**, 2283 (1969), and references therein.

[9] N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

[10] W. B. Hammond and N. J. Turro, *J. Amer. Chem. Soc.*, **88**, 2880 (1966).

[11] N. J. Turro and W. B. Hammond, *Tetrahedron*, 6017 (1968).

[12] N. J. Turro, S. S. Edelson, J. R. Williams, and T. R. Darling, *J. Amer. Chem. Soc.*, **90**, 1926 (1968).

[13] N. J. Turro and J. R. Williams, *Tetrahedron Lett.*, 321 (1969).

[14] N. J. Turro and S. S. Edelson, *J. Amer. Chem. Soc.*, **90**, 4499 (1968).

[15] A. W. Fort, *ibid.*, **84**, 4979 (1962).

[16] R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 129 (1963).

[17] R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc., C*, 473 (1967).

and 1360 cm^{-1} (*gem*-dimethyl), 725 cm^{-1} (>C=C<); nmr (CCl_4–TMS) δ 6.36–6.13 (m, 2 H), 4.65 (d, 1 H, J = 5 Hz), 4.29 (s, 1 H), 2.81 (d of *q*, 1 H, J = 7, 5 Hz), 0.89 (s, 3 H), 0.88 (d, 3 H, J = 7 Hz), 1.26 (s, 3 H); mass spectrum (75 eV) *m/e* (rel intensity) 166 (M^+, 37), 151 (15), 123 (6), 110 (12), 96 (81), 95 (67), 81 (100), 70 (31), 68 (13), 67 (22), 55 (23), 53 (17), 42 (28), 41 (65), 39 (64).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.10; H, 8.67.

From nmr, **5** appears to be a single isomer; however, of the four possible isomers, we do not know which isomer we have isolated.

1,1,2,6,6-Pentamethyl-5-oxo-4-oxaspiro[2.3]hexane (6).—To a 10% solution of dimethylketene (*ca.* 30 mmol) in CH_2Cl_2 was added a CH_2Cl_2 solution of **4**[18] (*ca.* 20 mmol). The solution was allowed to stand for 6 days at −78°. The resulting solution was concentrated and analyzed by vpc (6 ft × $^1/_4$ in., 22% Carbowax 20M, Chromosorb P, 200°, 120 cc of He/min). The major product was collected and identified as adduct **6** by the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1830 (C=O), 1385 and 1365 cm^{-1} (*gem*-dimethyl); nmr (CCl_4–TMS) δ 1.39 (s, 3 H), 1.29 (s, 3 H), 1.13 (s, 3 H), 1.09 (s, 3 H), 1.06 (d, 3 H, J = 7 Hz), 0.82 (q, 1 H, J = 7 Hz); mass spectrum (75 eV) *m/e* (relative intensity) 168 (3, M^+), 153 (2), 124 (1) 123 (2), 108 (7), 70 (100), 55 (25), 42 (41).

5,5-Dimethyl-4-isopropylidene-2-trichloromethyl-1,3-dioxolane (8).—A dilute (<1%) CH_2Cl_2–*n*-pentane solution (10 ml) of tetramethylcyclopropanone was mixed with chloral (1 ml, 10.3 mmol) and left at room temperature overnight. 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, 210 and 175°) then resulted in the isolation of **8**: ir $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; nmr (CCl_4–TMS) δ 1.46 (s, 3 H), 1.63 (s, 6 H), 1.67 (s, 3 H), 5.39 (s, 1 H); mass spectrum (75 eV) *m/e* (rel intensity) 258 (M^+, 8), 153 (2), 141 (33), 131 (5), 112 (7), 97 (10), 95 (100), 84 (51), 69 (50), 67 (16), 55 (15), 44 (39), 43 (34), 41 (32), 40 (31), 39 (12).

Registry No.—**2**, 24165-15-9; **3**, 24165-11-5; **5**, 24165-12-6; **6**, 24165-13-7; **8**, 24165-14-8.

[18] N. J. Turrc and R. B. Gagosian, *J. Amer. Chem. Soc.*, in press.

Glycidyltrimethylammonium Chloride and Related Compounds

JAMES D. MCCLURE

Shell Development Company, Emeryville Research Center, Emeryville, California 94608

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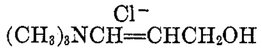
In 1904, Schmidt and Hartmann reported[1] obtaining glycidyltrimethylammonium chloride (I) as a noncrystallizable syrup of unspecified epoxide content by reacting epichlorohydrin with excess trimethylamine in ethanolic solution. The yield was low and the main product was the bis salt, 2-hydroxypropane-1,3-bis-(trimethylammonium chloride). Two decades earlier, Reboul had claimed[2] that the viscous syrup which was isolated when equal volumes of epichlorohydrin and triethylamine were heated to 100° was the homologous glycidyltriethylammonium chloride.

More recently a patent has issued to Paschall of the Corn Products Co. which claims the use of the product[3] from the interaction of epichlorohydrin with trimethylamine for the etherification of starch. According to Paschall, I was obtained[3] as a viscous syrupy distillation residue by treating epichlorohydrin with trimethylamine in aqueous solution at 25°. We have found that the syrup obtained by Paschall's procedure has only 40–60% of the theoretical epoxy oxygen value. On standing for 24 hr at 25°, the epoxide content declined to about half of its original value and, after 1 week at 25°, no significant (<5%) amount of epoxide remained. In a recent publication,[4] Burness has observed that reaction of epichlorohydrin with trimethylamine in acetonitrile at 25° affords N-(3-hydroxy-1-propenyl)trimethylammonium chloride (II, 87% yield) rather than I. We now report the preparation of pure, crystalline, stable glycidyltrimethylammonium chloride (I) for the first time.



$$\overset{Cl^-}{(CH_3)_3NCH{=}CHCH_2OH}$$

II

Results

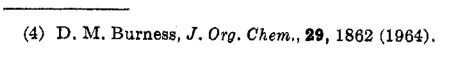
Glycidyltrimethylammonium Chloride.—The reaction of epichlorohydrin and trimethylamine to form I is best carried out in an aprotic solvent in which **I** is essentially insoluble. With excess epichlorohydrin as solvent (4.5:1 mole ratio), the reaction takes place very readily at 25° and I is formed in nearly quantitative yield and conversion. The product, a hygroscopic sharp-melting white crystalline material, is of 98% or better purity on the basis of epoxide content. When the reaction is conducted in other dry aprotic oxygenated solvents such as ethers, ketones, and esters, product of 95–97% epoxide content is isolated in nearly quantitative yield but only 50–75% conversion. The results of several experiments in which 0.25 mol of each reactant was stirred at 25–30° in 100–125 ml of the stipulated solvent for the specified period of time are summarized in Table I. The rate of the reaction is considerably greater in acetone (ϵ 21) than in other oxygenated aprotic solvents of lower dielectric constant (ϵ 4–7). In hexane (ϵ 1.9) the reaction proceeds at such a slow rate as to be impractical although product of good quality is obtained. In contrast, when the

TABLE I

REACTION OF EPICHLOROHYDRIN WITH TRIMETHYLAMINE

(0.25 mol of each reactant in 100–125 ml of solvent at 25–30°)

Solvent	Reaction time, hr	% conversion of epichlorohydrin	% yield of I	% purity (epoxide)
Acetone	35	74	97	96
Tetrahydrofuran	60	60	95	96
Dimethoxyethane	60	56	97	97
Ether	60	40	97	97
Ethyl Acetate	35	40		95
Hexane	60	15	98	96
Ethanol	16	95		20



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[1] E. A. Schmidt and H. Hartmann, *Ann.*, **337**, 116 (1904).

[2] E. Reboul, *Compt. Rend.*, **93**, 423 (1881).

[3] E. F. Paschall, U. S. Patent 2,876,217 (1959).

[4] D. M. Burness, *J. Org. Chem.*, **29**, 1862 (1964).