TABLE I
PRODUCT DISTRIBUTION FROM OXYMERCURATION-REDUCTION (eq 2)

Solvent	R	R'	Yield, %	% 4	5	6	7
8% H_2O in THF	H	H	37[a]	73.5	24.6	0.9	1.0
50% H_2O in THF	H	H	86	78.2	19.6	0.9	0.8
H_2O	H	H	84	83.6	15.1	0.7	0.6
20% H_2O in glyme	H	H	78	86.4	12.6	0.6	0.4
5% H_2O in DMSO	H	H	[b]	90.5	1.6	3.3	4.6
20% H_2O in CH_3CN	H	H	78	94.0	6.0	0	0
5% H_2O in CH_3CN	H	H	83	96.3	3.7	0	0
CH_3OH	H	CH_3	92	84.4	15.6	0	0
AcOH	H	Ac	95	82.0	6.8	4.4	6.8
40% H_2O in THF	CH_3	H	85	86.8	13.2	0	0
50% H_2O in THF	CH_3	H	92	89.0	11.0	0	0
5% H_2O in DMSO	CH_3	H	[b]	88.8	11.2	0	0
5% H_2O in CH_3CN	CH_3	H	93	94.0	6.0	0	0
AcOH	CH_3	Ac	87	93.6	6.4	0	0
25% H_2O in THF	Ac	H	95	70.0	30.0	0	0
75% H_2O in THF	Ac	H	95	70.5	29.5	0	0
5% H_2O in DMSO	Ac	H	[b]	85.6	3.3	8.6	2.5
5% H_2O in CH_3CN	Ac	H	95	96.0	4.0	0	0
CH_3OH	Ac	CH_3	90	74.5	25.5	0	0
AcOH	Ac	Ac	95	92	8	0	0

[a] The reaction is quite slow under these conditions; 58% of starting material recovered after 33 hr. [b] Yields were not determined owing to difficulty in separating solvent from products.

mation of 1,3 derivative can be ascribed to the inductive effect of the ring substituent. Halpern and Tinker[8] have demonstrated that oxymercuration of **1** occurs at about one-tenth the rate for cyclohexene, and there is thus no kinetic basis for anticipating stereospecific reaction of this system.[4]

Experimental Section

Oxymercuration and Reduction.—The olefin was added in one portion to a stirred solution of solvent and mercuric acetate. The reactions were run at 25°, and in general for 0.5 hr after the disappearance of the colloidal yellow mercuric oxide (not formed in nonaqueous solvents or pure water). The reactions for the most part were rapid, requiring only a few minutes to become colorless. The reactions in acetonitrile (5% H_2O) were fast (4 min to decolorize). DMSO, glyme, and THF containing small amounts of water required longer times for reaction.

Reduction was accomplished by using the sodium borohydride procedure of Brown and Geoghegan.[9] The aqueous base used in this method causes rapid hydrolysis of the acetate esters; this can be avoided by omitting the base and using excess borohydride.

The mercury was removed by filtration through Celite, the aqueous solution saturated with salt and extracted several times with ether. The combined ether extracts were dried with magnesium sulfate and evaporated. The diols thus obtained were taken up in pyridine and treated with excess acetic anhydride. The diacetates were analyzed using a 9 m × 3.2 mm 15% Carbowax 20M column at 152°. Retention times (RT) in minutes for these derivatives follow: **4**, 86; **5**, 100; **6**, 66; **7**, 62. The methoxy alcohols formed by hydroxymercuration of **2** or methoxymercuration of **1** were analyzed directly using the same column at 132°: **4**, 50.5; **5**, 45.6; **6**, 25; **7**, 19. The starting materials 2-cyclohexenol (**1**),[4,10] 3-methoxycyclohexene (**2**),[4] and 2-cyclohexenyl acetate (**3**)[11] have been described previously.

Product Assignments.—Commercial samples of *cis,trans*-1,2-cyclohexanediol and *cis,trans*-1,3-cyclohexanediol were converted into the diacetate derivatives. Literature procedures were used to prepare *trans*-1,2-diol,[12] *trans*-1,3-diol,[13] and *trans*-2-methoxycyclohexanol.[14] Jones oxidation of the latter gave 2-methoxycyclohexanone (96%), which in turn was reduced by $LiAlH_4$ in ether to give a mixture (nearly equal amounts) of the *cis* and *trans* alcohols. *trans*-3-Methoxycyclohexanol was obtained by the procedure of Eliel and Brett.[15] All compounds exhibited the anticipated nmr and ir spectral properties.

Registry No.—2-Cyclohexenol, 822-67-3.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation (GP 6043).

(8) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).
(9) H. C. Brown and P. Geoghegan, Jr., *ibid.*, **89**, 1522 (1967).
(10) R. Willstätter and E. Sonnenfeld, *Chem. Ber.*, **46**, 2952 (1913).
(11) H. J. Shine and J. R. Slagle, *J. Amer. Chem. Soc.*, **81**, 6309 (1959).
(12) A. C. Cope, H. E. Johnson, and J. S. Stephenson, *ibid.*, **78**, 5599 (1956).
(13) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2103 (1959).
(14) S. Winstein and R. B. Henderson, *J. Amer. Chem. Soc.*, **65**, 2196 (1943).
(15) E. L. Eliel and T. J. Brett, *J. Org. Chem.*, **28**, 1923 (1963).

Convenient Synthesis of 2,2-Dimethylcyclobutanone

WILLIAM C. AGOSTA AND DAVID K. HERRON

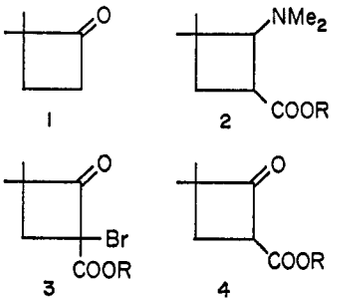
Laboratories of the Rockefeller University, New York, New York 10021

Received February 13, 1969

In connection with another investigation we required a convenient source of 2,2-dimethylcyclobutanone (**1**). There are two previously recorded preparations of this substance, the first[1] being the reaction of dimethylketene with ethylene at 200 atm pressure, and the second[2] involving addition of 2 equiv of diazomethane to dimethylketene. Neither of these seemed suitable for our purposes; the first requires pressure equipment not conveniently available, while the second gives largely the isomeric 3,3-dimethylcyclobutanone, from which the desired minor product **1** is difficultly separable. We describe below a useful preparative route to **1** from *t*-butyl acrylate and the dimethylenamine of isobutyraldehyde. Although four steps are involved from commercially available

(1) H. Bestian and D. Guenter, *Angew. Chem.*, **75**, 841 (1963).
(2) J.-M. Conia and J. Salaün, *Bull. Soc. Chim. Fr.*, 1957 (1964).

materials, the reactions proceed in high yield (50% over-all) and may be carried out quickly with little intermediate purification.

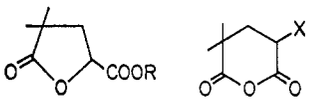


1 2 3 4

a, R = Me
b, R = CMe_3

The cycloaddition of acrylic esters to isobutyraldehyde enamine leads readily to amino esters **2**.[3] We have used both the previously known[3] methyl ester (**2a**) and the corresponding *t*-butyl ester (**2b**), finally converting the latter to **1**. The synthetic problem is then simply conversion of a dimethylamino group to carbonyl oxygen and complete elimination of an ester function. The first of these operations was smoothly effected by oxidation with bromine.[4] An aqueous solution of the amino ester buffered at pH 6 readily absorbed bromine to give the bromoketo ester (**3**). A second product accompanying **3a** is discussed later; this side reaction was absent in the *t*-butyl series, and **3b** could be obtained in good yield. The structure of **3** is clear from subsequent transformations, as well as completely appropriate spectroscopic properties. The extraneous bromine atom in bromoketo ester **3** was next removed by reduction with zinc dust in glacial acetic acid to furnish keto ester **4**. A second side product obtained in small amount in this reduction is also treated below; once again the side reaction occurred only in the methyl ester series.

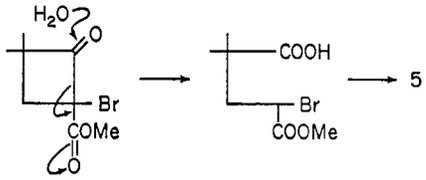
We were unable to define acidic conditions which favored ester hydrolysis in **4a** rather than ring opening. While this result is in agreement with recent experience elsewhere,[5] it contrasts with an early description of the successful hydrolysis and decarboxylation in acid of a 2-carbethoxycyclobutanone.[6,7] Similarly, mildly basic hydrolysis of **4a** gave only open-chain products; exposure of **4a** to 1.1 equiv of bicarbonate in methanol at room temperature, for example, led to a mixture of monomethyl and dimethyl 2,2-dimethylglutarate in 87% yield. On the other hand, acid-catalyzed pyrolysis[8] of the *t*-butyl ester **4b** proceeded most satisfactorily. At 138° **4b** lost isobutylene and carbon dioxide to give 2,2-dimethylcyclobutanone (**1**), which was characterized both by its ir and nmr spectra[2] and by preparation of its known 2,4-dinitrophenylhydrazone.[1]



5, R = Me
8, R = H

6, X = H
7, X = Br

We now describe two side products encountered in the methyl ester series. The first arose in variable yield (up to 18%) in the bromine oxidation of **2a** and appeared to be favored at the expense of **3a** if the reaction mixture, which became heterogeneous as oily **3a** separated, was stirred vigorously. The two products were readily separated by fractional distillation, and spectroscopic and analytical data for the side product suggested that it was lactone ester **5**. There was some uncertainty in this conclusion, however, for the nmr spectrum of this substance showed a six-proton singlet for the geminal methyl groups, and the ir spectrum (carbon tetrachloride) had three carbonyl absorption bands, at 1800, 1775, and 1750 cm^{-1}. The problem was settled by independent synthesis of **5**. Direct bromination of 2,2-dimethylglutaric anhydride (**6**)[9] gave α-bromo anhydride **7**, treatment of which first with hot aqueous sodium hydroxide and then with hydrochloric acid furnished lactone carboxylic acid **8**. Diazomethane converted **8** into its methyl ester **5** without difficulty, and this substance proved to be identical with the observed side product. Apparently **5** arises in the bromination reaction by slow hydrolytic cleavage of **3a** followed by intramolecular displacement of bromide ion.



Occurrence of the second side product is rather more interesting, although its origin has not been clearly traced. If **3a** was not rigorously purified before reaction with zinc in acetic acid, **4a** was accompanied by 5–15% of an isomeric methyl ester. This isomer was easily purified by vpc, after which it showed spectroscopic properties indicative of a conjugated enol ether [ir 1710 (s), 1625 (s) cm^{-1}; nmr δ 6.98 (t, J = 1.5 Hz, 1 H); and uv λ_{max} 253.5 mμ (ϵ 11,000)]. The data point to the carbomethoxydihydrofuran **10**, a conclusion substantiated by direct comparison of the side product with an authentic sample of **10**.[10] While we have been unable to isolate the precursor of **10**, which must accompany **3a** and **5** in the bromine oxidation, we suggest that the required transformations can be explained starting with an intermediate such as alcohol **11**. We emphasize that **11** has not been isolated and that other precursors, also plausibly present in the reaction mixture, could be advanced in its stead. Ring contraction in **11** would lead to the cyclopropylaldehyde **12**, a reasonable rearrangement in light of

(3) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961); **29**, 801 (1964).

(4) The conditions used were based on the general study of N. C. Deno and R. E. Fruit, Jr., *J. Amer. Chem. Soc.*, **90**, 3502 (1968).

(5) K. C. Brannock, R. D. Burpitt, and J. G. Thweatt, *J. Org. Chem.*, **29**, 940 (1964).

(6) A. Michael, *Ber.*, **33**, 3731 (1900).

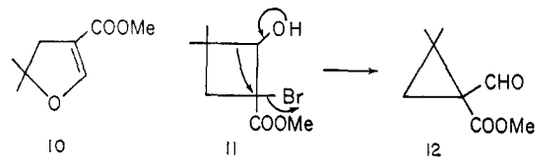
(7) We find, however, that from its nmr spectrum (see Experimental Section) the 2,4-dinitrophenylhydrazone of **4a**, formed under the usual acidic conditions, is indeed a cyclobutanone derivative rather than a glutaric acid hydrazide. The compound is identical with the hydrazone previously obtained[6] from the dimethylenamine of **4a**.

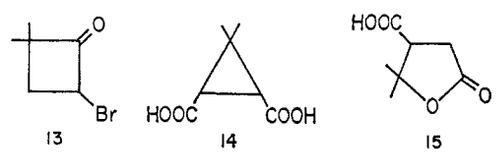
(8) D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1286 (1944); R. S. Yost and C. R. Hauser, *ibid.*, **69**, 2325 (1947); W. B. Renfrow and G. B. Walker, *ibid.*, **70**, 3957 (1948).

(9) E. Rothstein and W. G. Schofield, *J. Chem. Soc.*, 4566 (1965).

(10) F. Korte, K.-H. Büchel, D. Scharf, and A. Zschocke, *Chem. Ber.*, **92**, 884 (1959). We thank Professor Friedhelm Korte and Dr. Heinrich Wamhoff, University of Bonn, for generous samples of both **10** and the corresponding carboxylic acid.

the facility with which the parent bromo ketone (**13**) undergoes Favorskii rearrangement.[11] Acid-catalyzed transformation of **12** to **10** is mechanistically reasonable and has venerable analogy in the rearrangement of *cis*- or *trans*-caronic acid (**14**) to terebic acid (**15**).[12]





Experimental Section

Materials and Equipment.—Isobutyraldehyde dimethylenamine (N,N-dimethylisobutenylamine, K and K Laboratories), methyl acrylate (practical, Matheson Coleman and Bell), and *t*-butyl acrylate (Borden Chemical Co., Monomer–Polymer Laboratories) were used without further purification. Vpc was carried out using a Varian Aerograph Model 700 Autoprep with a 20 ft × 0.25 in. stainless steel column packed with 30% FFAP on Chromosorb W, and operated at 180° with a helium carrier gas flow rate of 100 ml/min. Unless otherwise noted, both ir and nmr spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer 237B spectrophotometer and the latter on a Varian A-60 spectrometer. Distillations were carried out under nitrogen.

***t*-Butyl 2-(Dimethylamino)-3,3-dimethylcyclobutanecarboxylate (2b).**—*t*-Butyl acrylate (16.25 g), isobutyraldehyde dimethylenamine (34.10 g), and 40 ml of acetonitrile were heated at reflux under nitrogen for 54 hr. Acetonitrile and excess enamine were removed by distillation at atmospheric pressure and the remainder was distilled at reduced pressure to give 18.06 g (63%) of product: bp 45–47° (0.08 mm); ir 2855, 2805, 2760, 1725 (s), 1365, 1145 cm^{-1}; nmr δ 2.72–2.18 (m, 3 H), 2.02 (s, 6 H), 1.70 (m, 1 H), 1.41 (s, 9 H), 1.12, 1.06 (two s, 6 H).

Anal. Calcd for $C_{12}H_{25}O_2N$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.54; H, 11.37; N, 6.05.

Methyl 1-Bromo-2-oxo-3,3-dimethylcyclobutanecarboxylate (3a).—Amino ester **2a**[3] (21.7 g) was dissolved in 600 ml of 2 *M* acetate buffer (pH 6). Bromine (43 g) was added dropwise with mechanical stirring and cooling below room temperature. Excess bromine was destroyed with solid $NaHSO_3$ about 15 min after bromine addition was complete, and the reaction mixture was extracted with ether. The ether extracts were washed with 0.5 *M* HCl, 0.6 *M* $NaHCO_3$, water, and brine, and dried over Na_2SO_4. Evaporation of ether gave 17.3 g (63%) crude product, which was distilled: bp 46–48° (0.1 mm); mp 31–33°; ir 1801 (s), 1730 (s), 1430, 1250 (s), 1120, 1000 cm^{-1}; nmr δ 3.80 (s, 3 H), 3.00 (d, J = 13 Hz, 1 H), 2.28 (d, J = 13 Hz, 1 H), 1.44 (s, 3 H), 1.26 (s, 3 H).

Anal. Calcd for $C_8H_{11}O_3Br$: C, 40.87; H, 4.72. Found: C, 41.13; H, 4.78.

***t*-Butyl 1-Bromo-2-oxo-3,3-dimethylcyclobutanecarboxylate (3b).**—*t*-Butyl amino ester **2b** (32.9 g) was oxidized as described above for **2a** to give 35.13 g (88%) crude product, which from nmr analysis contained very little impurity (no absorption below 3.1 ppm). Distillation gave an analytical sample: bp 71–73° (0.5 mm); ir 1798 (s), 1775 (m), 1725 (s), 1370 (s), 1255 (s), 1160 (s); nmr δ 2.92 (d, J = 13.5 Hz, 1 H), 2.22 (d, J = 13.5 Hz, 1 H), 1.48, 1.42 (two s, 12 H), 1.25 (s, 3 H).

Anal. Calcd for $C_{11}H_{17}O_3Br$: C, 47.66; H, 6.18. Found: C, 47.76; H, 6.24.

Methyl 3,3-Dimethyl-2-oxocyclobutanecarboxylate (4a).—A solution of slightly impure bromoketo ester **3a** [(671 mg, bp 72–87° (2.0 mm)] in 25 ml of glacial acetic acid was chilled in an ice bath. Zinc dust (1.0 g) was added with vigorous stirring and the mixture was allowed to come to room temperature as the stirring continued for 30 min. The mixture was filtered and the excess zinc washed with ether and water. The resulting solution was extracted with ether, and the ether extracts were washed with water, 0.6 *M* $NaHCO_3$, water, and brine and were dried over Na_2SO_4. Evaporation of ether gave 340 mg (76%) of crude keto ester contaminated with about 5% of dihydrofuran **10**: ir 1795 (s), 1735 (s), 1315, 1205, 1170 cm^{-1}; nmr (parts per million downfield from external tetramethylsilane in CCl_4) 4.12 (dd, J_1 = 10 Hz, J_2 = 6.5 Hz, 1 H), 3.68 (s, 3 H), 2.30–1.75 (m, 2 H), 1.20 (s, 6 H). When analytically pure bromoketo ester was reduced, no **10** was formed.

A 2,4-dinitrophenylhydrazone was prepared for analysis: mp 132–133° from methanol (lit.[5] mp 128.5–130°); nmr ($CDCl_3$; parts per million downfield from external tetramethylsilane in $CHCl_3$) 11.4 (broad s, 1 H), 8.95 (d, J = 2 Hz, 1 H), 8.20 (dd, J_1 = 9 Hz, J_2 = 2 Hz, 1 H), 7.80 (d, J = 9 Hz, 1 H), 4.23 (dd, J_1 = 10 Hz, J_2 = 6 Hz, 1 H), 3.84 (s, 3 H), 2.24–1.93 (m, 2 H), 1.33 (s, 6 H).

Anal. Calcd for $C_{14}H_{16}O_6N_4$: C, 49.99; H, 4.80; N, 16.66. Found: C, 49.80; H, 4.97; N, 16.91.

Methyl 4,5-Dihydro-5,5-dimethyl-3-furoate (10).—Reduction of crude bromoketo ester **3a** with zinc dust always gave 5–15% of dihydrofuran **10**. Preparative vpc destroyed the keto ester but gave pure **10** (retention time 24 min); ir 1710 (s), 1625 (s), 1175, 1090 cm^{-1}; nmr (parts per million downfield from external tetramethylsilane in CCl_4) 6.98 (t, J = 1.5 Hz, 1 H), 3.56 (s, 3 H), 2.53 (d, J = 1.5 Hz, 2 H), 1.32 (s, 6 H); uv (CH_3OH) λ_{max} 253.5 mμ (ϵ 11,000).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: 61.61; H, 7.56.

The vpc retention time and ir, uv, and nmr spectra of this material were identical with those of an authentic sample.[10]

Hydrolysis of Methyl 3,3-Dimethyl-2-oxocyclobutanecarboxylate (4a). A. Basic Hydrolysis.—Keto ester **4a** (4.74 g) was stirred at room temperature under nitrogen for 23 hr with 20 ml of methanol, 60 ml of water, and 2.90 g (1.1 equiv) of $NaHCO_3$. The reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with water, dried over Na_2SO_4, and evaporated to give 2.04 g of colorless oil, ir and nmr spectra identical with those of authentic dimethyl 2,2-dimethylglutarate. Acidification of the reaction mixture followed by ether extraction gave 2.70 g of colorless oil: ir 3300–2700 (broad), 1740 (s), 1701 (s); nmr (parts per million downfield from external tetramethylsilane in CCl_4) 10.4 (s, 1 H), 3.57 (s, 3 H), 2.47–1.67 (m, 4 H), 1.17 (s, 6 H). Esterification of this material with diazomethane gave dimethyl 2,2-dimethylglutarate.

B. Acidic Hydrolysis.—The keto ester **4a** (820 mg) was heated at reflux with 1.6 ml of 6 *M* HCl for 1.5 hr and the reaction mixture was extracted with ether. The ether extracts were washed with water and brine and dried over Na_2SO_4. Evaporation of ether gave 746 mg of crude brown oil: ir 3400–2400 (broad), 1735 (w), 1710 (s). There was no cyclobutane carbonyl absorption.

***t*-Butyl 3,3-Dimethyl-2-oxocyclobutanecarboxylate (4b).**—*t*-Butyl bromoketo ester **3b** (5.93 g) was reduced as described above for **3a** to give 4.31 g (100%) of crude product which showed no impurities in its nmr spectrum. Distillation gave analytically pure material: bp 80.2° (2.8 mm); ir 1780 (s), 1724 (s), 1365 (m), 1150 (s); nmr δ 4.05 (dd, J_1 = 10 Hz, J_2 = 7 Hz, 1 H), 2.40–1.75 (m, 2 H), 1.41 (s, 9 H), 1.22 (s, 6 H).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.63; H, 9.15. Found: C, 66.81; H, 9.33.

2,2-Dimethylcyclobutanone (1).—*t*-Butyl keto ester **4b** (9.86 g) and *p*-toluenesulfonic acid monohydrate (40 mg) were heated with an oil bath in a distillation apparatus under nitrogen. Smooth gas evolution began at a bath temperature of 138°, and product began to distil. The reaction was complete in 15 min, during which time bath temperature increased to 152° and 4.31 g (91%) very slightly impure product distilled. Redistillation through a short Vigreux column gave pure material, bp 113.5–114° (760 mm). The spectroscopic properties of this material were in complete agreement with literature values.[2]

A 2,4-dinitrophenylhydrazone was prepared: mp 140.5–141.5° from methanol (lit.[1] mp 140–141°).

2,2-Dimethyl-4-bromoglutaric Anhydride (7).—A mixture of 2,2-dimethylglutaric anhydride (**6**)[9] (1.29 g) and red phosphorus

(11) Treatment of **13** with hot water or liquid ammonia or aqueous carbonate at 50° brings about quantitative Favorskii rearrangement.[2]

(12) A. Baeyer and W. Ipatiew, *Ber.*, **29**, 2796 (1896).

(about 10 mg) was heated to 85–90° and treated over 5 min with bromine (1.31 g). Direct crystallization of the product from benzene gave 610 mg. Several recrystallizations from benzene–cyclohexane followed by sublimation gave an analytical sample: mp 79–81°; ir 1823 (m), 1780 (s), 1024 (s) cm^{-1}; nmr δ 4.72 (t, J = 8 Hz, 1 H), 2.38 (d, J = 8 Hz, 2 H), 1.47 (s, 3 H), 1.43 (s, 3 H).

Anal. Calcd for $C_7H_9O_3Br$: C, 38.03; H, 4.10; Br, 36.15. Found: C, 37.97; H, 4.12; Br, 35.89.

2,2-Dimethyl-4-hydroxyglutaric Acid Lactone (8). A. Authentic Sample.—A mixture of bromo anhydride **7** (150 mg) and 10 ml of 5% aqueous sodium hydroxide was heated at reflux under nitrogen for 3 hr. The resulting clear solution was taken to dryness *in vacuo;* the residue was taken up in hydrochloric acid, and the solution was again taken to dryness. Extraction of the residue with several portions of hot benzene gave 89 mg (90%) of crude product. Several recrystallizations from benzene–cyclohexane gave an analytical sample: mp 82–84°; ir (KBr disk) 3600–2800 (broad), 1780 (s), 1750 (s), 1178 (s), 1165 (s), 1060 (s) cm^{-1}; nmr ($CDCl_3$) δ 10.71 (s, 1 H), 4.95 (t, J = 8 Hz, 1 H), 2.42 (dd, J_1 = 6 Hz, J_2 = 8 Hz, 2 H), 1.31 (s, 6 H).

Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.16; H, 6.35.

B. By Saponification of 5.—A solution of lactone methyl ester **5** (300 mg) in 40 ml of methanol containing 6.9 ml of 0.5 *M* sodium hydroxide was kept overnight at room temperature under nitrogen and was then taken to dryness. The residue was taken up in water, acidified with concentrated HCl to pH 2, taken again to dryness, and then worked up as in A above. There was recovered 260 mg (94%) of crude crystalline product. Two recrystallizations gave a sample with melting point, mixture melting point, ir, and nmr spectra identical with those of an authentic sample.

2,2-Dimethyl-4-hydroxyglutaric Acid Lactone Methyl Ester (5). A. Authentic Sample.—A solution of lactone carboxylic acid **8** (50 mg) in 10 ml of ether was treated with excess ethereal diazomethane and allowed to remain at room temperature for 2 hr. The solution was taken to dryness and the product twice crystallized from benzene–cyclohexane: mp 49.5–50°; ir (KBr disk) 2950 (m), 1775 (s), 1760 (s), 1220 (ms), 1195 (ms), 1065 (s) cm^{-1}; (CCl_4) 2950 (m), 1800 (s), 1775 (ms), 1750 (ms), 1200 (ms), 1110 (m), 1070 (m) cm^{-1}; nmr δ 4.80 (t, J = 7.5 Hz, 1 H), 3.80 (s, 3 H), 2.29 (dd, J_1 = 7.5 Hz, J_2 = 6.5 Hz, 2 H), 1.25 (s, 6 H).

B. From Bromination of Amino Ester 2a.—Distillation of the crude bromination product described above gave a fraction of variable amount, bp 85–88° (0.3 mm), which spontaneously crystallized in the cold. Recrystallization of this material first from CCl_4 and then from benzene–cyclohexane gave stout needles, melting point, mixture melting point, and ir and nmr spectra identical with those of an authentic sample.

Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.97; H, 7.25.

Registry No.—**1**, 1192-14-9; **2b**, 20104-44-3; **3a**, 20104-45-4; **3b**, 20104-46-5; **4b**, 20104-47-6; **5**, 20104-48-7; **7**, 20104-49-8; **8**, 20104-52-3; **10**, 20104-53-4.

Acknowledgment.—It is a pleasure to acknowledge the aid of the National Science Foundation through Grant GB-137 and a graduate fellowship to D. K. H.

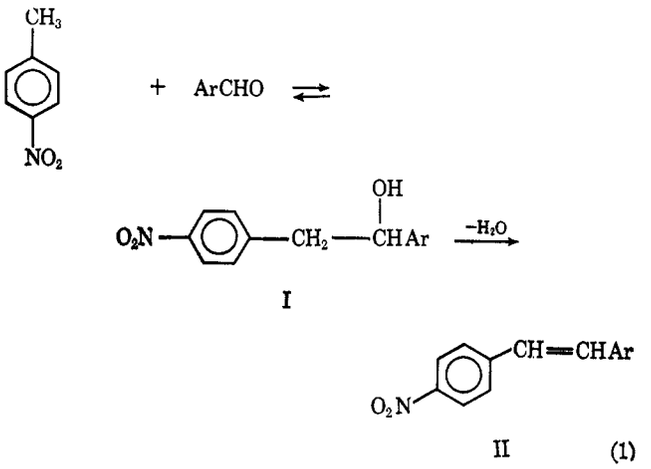
Condensation of *p*-Nitrotoluene with Aldehydes

W. J. FARRISSEY, JR., F. P. RECCHIA, AND A. A. R. SAYIGH

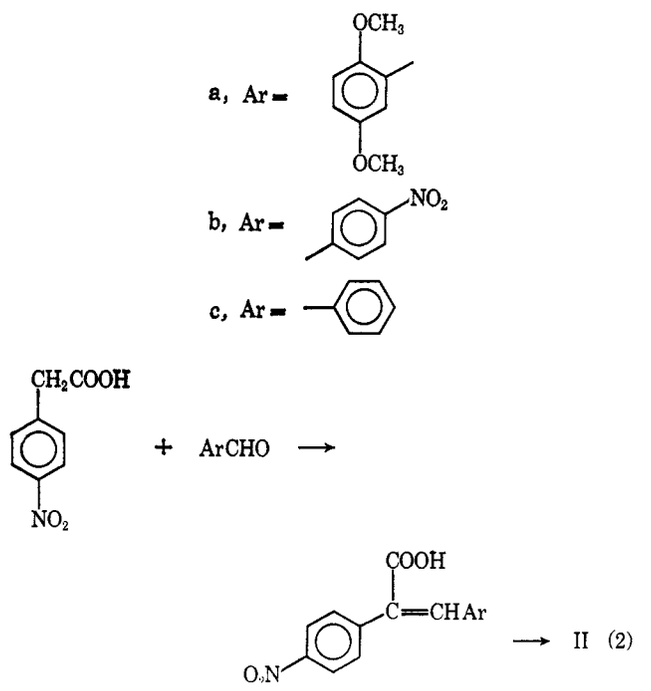
The Upjohn Company, Donald S. Gilmore Research Laboratories, North Haven, Connecticut

Received December 9, 1968

Base-catalyzed condensation reactions of *p*-nitrotoluene are complicated by the facile oxidation[1,2] and dimerization[2,3] of the *p*-nitrotoluene carbanion. Condensation with aldehydes has resulted in very poor yields of the desired stilbenes[4] (eq 1), and has led to the use of the condensation–decarboxylation sequence employing *p*-nitrophenylacetic acid[5] (eq 2).



(1)



(2)

Despite the unpromising past performance of the *p*-nitrotoluene carbanion in condensation reactions,[3,4] it was expected that the proper choice of solvent might improve the situation. That highly polar aprotic solvents can greatly assist a variety of anionic processes has been abundantly demonstrated in recent years.[2,6] Therefore, the condensation of *p*-nitrotoluene with aromatic aldehydes in dipolar aprotic solvent systems was investigated.

(1) T. Tsuruta, *et al.*, *Bull. Inst. Chem. Res., Kyoto Univ.*, **30**, 46, 47 (1952); *Chem. Abstr.*, **48**, 11369, 13376 (1954).

(2) G. A. Russell, A. J. Moye, E. G. Janzen, S. Mak, and E. R. Ralaty, *J. Org. Chem.*, **32**, 137 (1967).

(3) E. Borello and M. E. G. Locchi, *Ann. Chim.* (Rome), **43**, 25 (1953); *Chem. Abstr.*, **48**, 2015 (1954); F. W. Bergstrom, I. M. Granara, and V. Erickson, *J. Org. Chem.*, **7**, 98 (1942).

(4) L. Chardonnens and P. Heinrich, *Helv. Chim. Acta*, **22**, 1471 (1939); J. F. J. Dippy, L. T. Hogarth, H. B. Watson, and F. R. Williams, *J. Soc. Chem. Ind.*, **56**, 396 (1937).

(5) H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.*, **31**, 4146 (1966); A. A. R. Sayigh and H. Ulrich, U. S. Patent 3,363,004 (1968); R. Ketcham and D. Jambotkar, *J. Org. Chem.*, **28**, 1034 (1963), and references cited therein.

(6) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); A. Schreischeim, *et al.*, Belgian Patent 617,842; *Chem. Abstr.*, **59**, 3772 (1963).