Base-induced Reactions of 2-Substituted 2-Bromodimedones

Tadahiro WAKUI, Yoshio OTSUJI, and Eiji IMOTO

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai-shi, Osaka 591

(Received February 12, 1974)

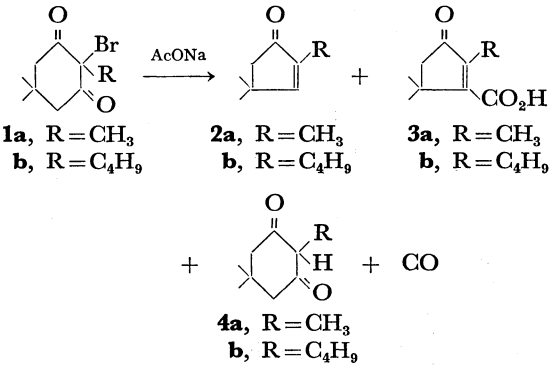
The reactions of 2-substituted 2-bromodimedones with various bases were studied. The behavior of the dimedones changed with the base and substituent attached to the dimedones. Treatment of 2-alkyl-2-bromodimedones (**1a** and **1b**) with a weak nucleophilic base such as sodium acetate afforded 2-alkyl-4,4-dimethyl-2-cyclopenten-1-ones (**2a** and **2b**), 2-alkyl-5,5-dimethyl-3-oxo-1-cyclopentene-1-carboxylic acids (**3a** and **3b**), 2-alkyl-5,5-dimethylcyclohexane-1,3-diones (**4a** and **4b**) and carbon monoxide. A similar treatment of 2,2-dibromodimedone (**7**) with the weak nucleophilic base gave 2,3-dibromo-4,4-dimethyl-2-cyclopenten-1-one (**8**), 2-bromo-5,5-dimethylcyclohexane-1,3,4-trione (**9**) and 2-bromodimedone (**10**). However, the reactions of **1a** and **7** with a strong nucleophilic base such as sodium ethoxide gave mainly the open-chain products, ethyl 3,3-dimethyl-5-oxoheptanoate (**5a**) and diethyl 3,3-dimethylglutarate (**11**). On treatment of **1a** with silver acetate, a debrominative dimerization occurred to produce the dimer **6**. The mechanisms of these reactions were discussed.

The preparation of substituted cyclopentenones has drawn considerable attention. One available method is the conversion of cyclohexane-1,3-dione derivatives into cyclopentenones. Spencer and co-workers[1,2] reported that the thermolysis of 2-acetoxy-2-alkylcyclohexane-1,3-diones gives carbon monoxide and 2-alkylcyclopentenones. However, an application of this method is limited because of the difficulty to prepare the acetoxydiones. Büchi and Egger[3] found that 2-chloro-2-(2-pentynyl)-cyclohexane-1,3-dione can be converted into 2-(2-pentynyl)-2-cyclopenten-1-one in an 80% yield upon treatment with sodium carbonate. Since 2-chlorocyclohexane-1,3-dione derivatives are readily accessible, this base-induced ring contraction seems to have a wide applicability, provided that the ring contraction is a general reaction. We recently found that the chemical behavior of 2-bromocyclohexane-1,3-diones varied remarkably with the nature of the base employed and also with the substituent attached to the diones. This paper deals with a systematic study on the reactions of 2-substituted 2-bromodimedones with various bases.

Results and Discussion

Reaction Products. The reactions of 2-substituted 2-bromodimedones with various bases were carried out in tetrahydrofuran (THF) or in ether, and the products were isolated and then characterized. The products isolated are summarized in Table 1.

The reaction of 2-bromo-2-methyldimedone (**1a**) with an equivalent of sodium acetate in THF under reflux afforded 2,5,5-trimethyl-2-cyclopenten-1-one (**2a**), 2,4,4-trimethyl-3-oxo-1-cyclopentene-1-carboxylic acid (**3a**) and 2-methyldimedone (**4a**). A similar reaction of 2-bromo-2-butyldimedone (**1b**) with sodium acetate gave the corresponding products, **2b**, **3b**, and **4b**. Evolution of CO was observed during the course of these reactions.



1a, R=CH_3 **2a**, R=CH_3 **3a**, R=CH_3
b, R=C_4H_9 **b**, R=C_4H_9 **b**, R=C_4H_9

4a, R=CH_3
b, R=C_4H_9

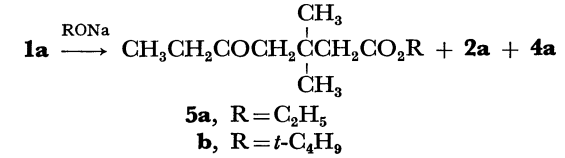
However, when **1a** was treated with two equivalents

Table 1. Reactions of 2-substituted 2-bromodimedones with bases in THF

Compd	Base	Reaction time, hr	Products (Yield, %)			
			Cyclopentenone	Cyclopentenone-carboxylic acid		Others
1a	AcONa	4	**2a** (21)	**3a** (37)		**4a** (7.5)
1b	AcONa	4	**2b** (35)	**3b** (15)		**4b** (5.3)
1a	C_2H_5ONa[a]	5	**3a** (5.6)		**5a** (64)	**4a** (9)
1a	*t*-C_4H_9ONa	5	**2a** (12)			**4a** (34)
1a	AcOAg	5	**2a** (17)	**3a** (10)	**6** (53)	**4a** (7.5)
1a	AcOAg	18	**2a** (19)	**3a** (3)	**6** (22)	**4a** (9)
7	AcONa	4	**8** (25)		**9** (16)	**10** (32)
7	Na_2CO_3	4	**8** (16)		**9** (10)	**10** (25)
7	$C_2H_5CO_2Na$	4	**8** (15)		**9** (13)	**10** (28)
7	C_2H_5ONa	5			**11** (38)	**10** (35)
7	AcOAg	5	**12** (24)			**10** (41)

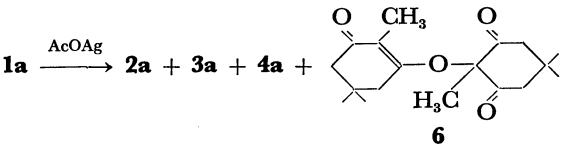
a) The reactions were carried out in ether instead of THF.

of sodium ethoxide, ethyl 3,3-dimethyl-5-oxoheptanoate (**5a**) was obtained as a major product along with small amounts of **2a** and **4a**.



5a, R=C_2H_5
b, R=t-C_4H_9

Treatment of **1a** with an equivalent of sodium t-butoxide gave **2a** and **4a**, but t-butyl ester (**5b**) could not be isolated. The reaction of **1a** with an equivalent of silver acetate in THF yielded a small amount of a dimeric product (**6**) along with **2a**, **3a** and **4a**.



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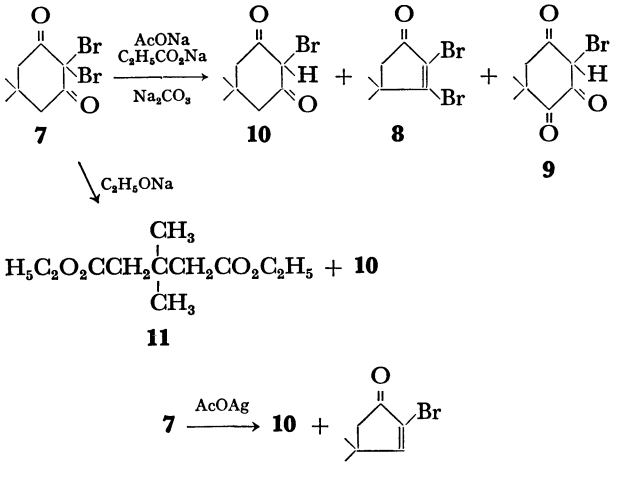
The reaction of 2,2-dibromodimedone (**7**) with various bases was then examined. Treatment of **7** with an equivalent of weak bases, such as sodium acetate, sodium propionate and sodium carbonate, in THF afforded 2-bromodimedone (**10**), 2,3-dibromo-4,4-dimethyl-2-cyclopenten-1-one (**8**) and 2-bromo-5,5-dimethylcyclohexane-1,3,4-trione (**9**). The reaction of **7** with two equivalents of sodium ethoxide in ether gave **10** and diethyl 3,3-dimethylglutarate (**11**). The reaction of **7** with an equivalent of silver acetate in THF yielded **10** and 2-bromo-4,4-dimethyl-2-cyclopenten-1-one (**12**).



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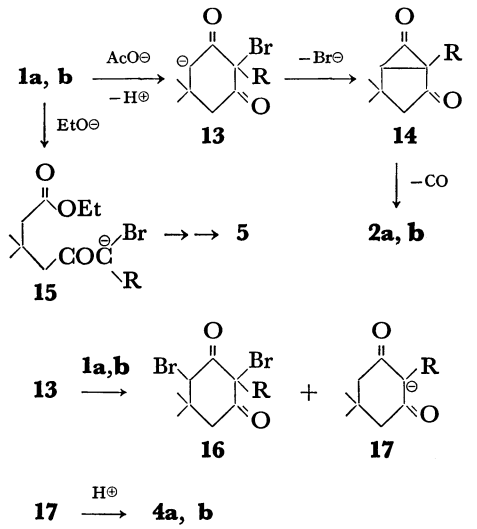
Determination of the Structures of the Products. The structures of the cyclopentenones **2a**, **2b**, **8**, and **12** were readily established from their IR and NMR spectra which exhibited absorptions and signals characteristic of the assigned structures (see Experimental): the IR and NMR spectral data of **2a** obtained in this investigation were identical with those reported.[1]

The structures of the cyclopetenonecarboxylic acids **3a** and **3b** were established by their IR, NMR, and UV spectra. The IR spectrum (KBr) of **3a** showed multiple absorptions characteristic of a carboxyl group at 3300—2500 cm^{-1}, carbonyl absorptions at 1710 and 1670 cm^{-1}, and an absorption due to the C=C bond at 1620 cm^{-1}. The NMR spectrum ($CDCl_3$–DMSO-d_6) of **3a** exhibited a singlet signal due to six protons of the two methyl groups at the 5-position at δ 1.34, and a singlet signal due to three protons of the methyl group at the 2-position at δ 1.88, a singlet signal due to two protons of the methylene function at the 4-position at δ 2.32, and a broad singlet signal due to one proton of the carboxyl group at the 1-position at δ 6.15. The UV spectrum of **3a** in 95% ethanol showed an absorption maximum at 243 nm (ε 9800), indicating that **3a** has a cyclopentenone skeleton.[4] These data are consistent with the structure assigned to **3a**. Similar spectral data were obtained for **3b**, confirming the assingned structure: the IR spectrum (KBr) showed absorptions at 3300—2600 (multiplet), 1710, 1680, and 1620 (C=C) cm^{-1}. The NMR spectrum (CCl_4) exhibited a singlet signal at δ 1.36 (six protons of the two methyl groups at the 5-position), multiplet signals at δ 0.8—2.3 (nine protons of the butyl group at the 2-position), a singlet signal at δ 2.32 (two protons of the methylene group at the 4-position) and a broad singlet signal centered at δ 9.1 (one proton of the carboxyl group at the 1-position). The UV spectrum in 95% ethanol showed an absorption maximum at 244 nm (ε 9300).

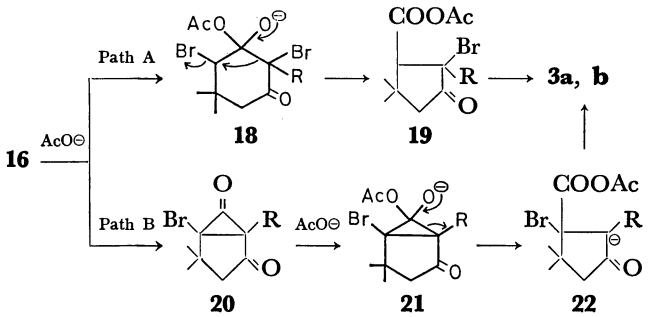
The IR and NMR spectral data of the dimer **6** obtained in this investigation were identical with those reported.[1] Additional evidence for the assigned structure was obtained from the fact that a mild treatment of **6** with aqueous hydrochloric acid afforded quantitatively 2-methyldimedone (**4a**). As a result of this chemical reaction, a fragment peak appeared at m/e 153 (corresponding to just a half of the molecule) in the mass spectrum. The structure of **9** was confirmed by a color reaction with ferric chloride, which demonstrated the enolizable property of the substance, and by the IR and NMR spectra. The structures of the esters **5a** and **11** were confirmed by comparison of the retention times in vpc with those of authentic samples.

Mechanistic Interpretation. From the results obtained we see that the kind and distribution of the products produced by the reactions of 2-bromodimedones with bases depend largely on the nature of the base as well as the substituent attached at the 2-position of dimedones.

The reactions of 2-alkyl-2-bromodimedones, **1a** and **1b**, with bases are discussed first. The yields of cyclopentenones **2a** and **2b** were high in the reactions with a weak nucleophilic base such as sodium acetate. The production of **2a** and **2b** was accompanied by the formation of cyclopentenonecarboxylic acids **3a** and **3b** and debrominated dimedones **4a** and **4b**. When **1a** was allowed to react with sodium ethoxide which possesses a relatively high nucleophilicity, an attack of ethoxide ion on a carbonyl carbon in the substrate predominated to produce mainly the open-chain product, **5**. The proposed mechanisms which qualitatively accomodate these results are represented in Schemes 1 and 2: since experimental difficulty in the separation of the products prevented a quantitative determination of the product distribution, the proposed



Scheme 1.



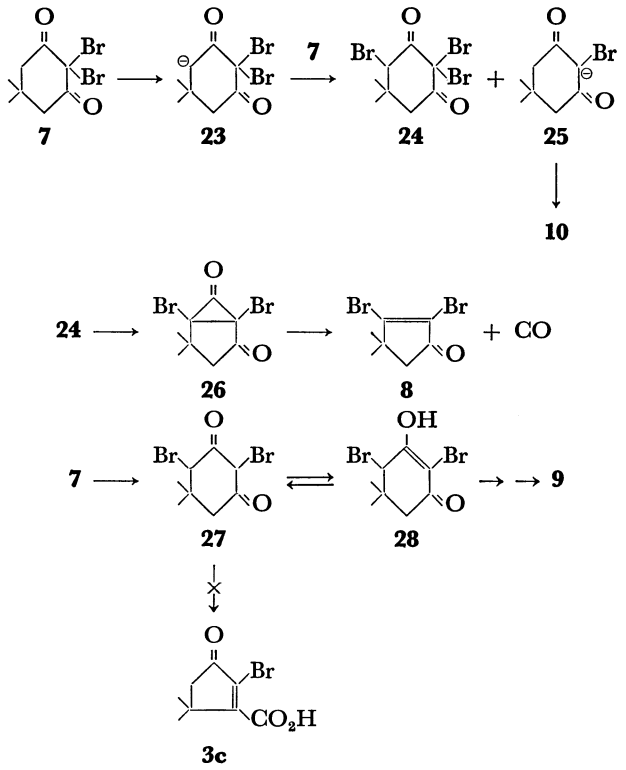
Scheme 2.

mechanisms might be inconsistent with the results given in Table 1.

A base of low nucleophilicity abstracts a proton from an active methylene group of **1a**, **b** to form carbanion **13**, which is then transformed into cyclopropanone intermediate **14** by elimination of bromide ion. The 1,3-elimination of hydrogen bromide of this sort has been postulated in the Favorskii rearrangement of α-bromoketones.[5] Decarbonylation from **14** affords the cyclopentenone **2a**, **b** (Scheme 1). The stabilized carbanion **13** would also react with **1a**, **b** to form the dibromide **16** and the carbanion **17** which on protonation yields **4a**, **b**. The transfer of bromonium ion from **1a**, **b** to **13** is possible, since bromine in **1a**, **b** is activated by the two adjacent carbonyl groups.

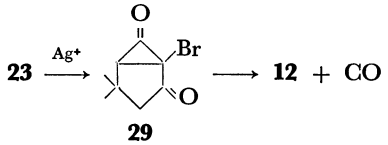
Two paths can be considered for the formation of **3a**, **b** (Scheme 2). Path A is a semibenzylic-type rearrangement[6] induced by an attack of base to the carbonyl carbon of **16** to form an intermediate **19** which is readily converted into **3a**, **b** by the dehydrobromination and the hydrolysis. Path B is the base-induced Favorskii-type rearrangement of **16** to produce **3a**, **b** through an intermediate **22**. We prefer path A to path B from the following considerations: (a) The reaction of **1a** with *t*-butoxide, which is a bulky strong base, exclusively affords **2a** without formation of **3a**. This result can be interpreted by assuming that a larger steric interaction between a substituent at the 2-position of **16** and base hinders an attack of the base on the carbonyl carbon of **16**. (b) If path B were to be taken, a compound produced by the decarbonylation from **20** should be obtained. However, such a product could not be isolated.

A possible mechanism for the reactions of **7** with weak bases is outlined in Scheme 3. In these reactions cyclohexane-1,3,4-trione (**9**) was obtained, but not 2-bromo-5,5-dimethyl-3-oxo-1-cyclopentene-1-carboxylic acid (**3c**, R=Br in **3**). This is understandable from the fact that 2-monosubstituted dimedone such as **27** which is a precursor of **3c** exists predominantly in the enol form such as **28**. The attack of weak bases on the enolized carbonyl carbon would be difficult. Consequently, the pathway leading to **3c** is prohibited, and **28** might be transformed into **9** through complex pathways involving oxidation.



Scheme 3.

An unusual reaction took place with the use of silver acetate. The reaction of **1a** with silver acetate gave the dimeric product **6**, whose yield increased with reaction time. However, the mechanism for the formation of **6** is yet uncertain. The reaction of **7** with silver acetate afforded the monobromocyclopentenone **12**. This may be accounted for by a strong affinity of silver ion to bromide ion, which promotes the formation of the cyclopropanone **29** from **23**.



Experimental

2-Bromo-2-methyldimedone (1a). Bromine (16.0 g, 0.1 mol) was added gradually to a stirred mixture of 15.4 g

(0.1 mol) of 2-methyldimedone (**4a**)[7] and 11.8 g (0.1 mol) of AcONa in 120 ml of $CHCl_3$–H_2O (6: 1) below 5 °C. The mixture was stirred for 1 hr, and the $CHCl_3$ layer was then separated. The aqueous layer was extracted with 50 ml of $CHCl_3$. The combined $CHCl_3$ solutions were dried (Na_2SO_4) and evaporated under reduced pressure. Recrystallization of the residue from $CHCl_3$–CCl_4 (1: 3) gave 19.5 g (84%) of **1a**; mp 102—104 °C. IR(KBr): 1720 and 1695 cm^{-1} (C=O). NMR($CDCl_3$) δ 1.12 (s, 6H, two CH_3's), 1.82 (s, 3H, CH_3–C(Br)–) and 2.70 (s, 4H, $-CH_2-C(Br)-CH_2-$).

Found: C, 46.52; H, 5.37%. Calcd for $C_9H_{12}O_2Br$: C, 46.37; H, 5.62%.

*2-Bromo-2-butyldimedone (**1b**).* Bromination of 2-butyldimedone[7] by a method similar to that described above gave **1b** in 78% yield; mp 97—99 °C; IR(KBr) 1710 and 1700 cm^{-1} (C=O).

Found: C, 52.46; H, 6.62%. Calcd for $C_{12}H_{19}O_2Br$: C, 52.38; H, 6.96%.

*Reaction of **1a** with AcONa.* A mixture of 1.0 g (4.3 mmol) of **1a** and 0.37 g (4.5 mmol) of anhydrous AcONa in 60 ml of THF was refluxed for 4 hr. The reaction mixture was poured into water, neutralized with 1 M HCl, and extracted with two 30 ml portions of ether. The combined ether extracts were washed with 5% Na_2CO_3, dried and evaporated to leave an oil. Distillation of the oil gave 0.11 g (21%) of (**2a**); bp 160—165 °C. IR (film): 1700 (C=O) and 1640 cm^{-1} (C=C). NMR (CCl_4): δ 1.19 (s, 6H, two CH_3's at the 4-position), 1.65 (d, J=1 Hz, 3H, **CH_3**–C=CH–), 2.12 (s, 2H, **$-CH_2-$**), and 6.92 (q, J=1 Hz, 1H, **H**–C=C–CH_3).

Found: C, 77.68; H, 9.58%. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74%.

Chromatography of the oil on silica-gel with $CHCl_3$ gave 50 mg (5%) of unchanged **1a**.

The Na_2CO_3 solution was neutralized with 1 M HCl and extracted with ether. The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica-gel with benzene–CCl_4 (1: 3). The earlier fractions gave 0.27 g (37%) of 5,5-dimethyl-2-methyl-3-oxo-1-cyclopentene-1-carboxylic acid (**3a**), which upon recrystallization from $CHCl_3$ afforded an analytical sample of mp 189—191 °C. Mass spectrum: *m/e* 168 (M^+), 140, 125, and 124.

Found: C, 64.53; H, 7.41%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

The latter fractions in the chromatography afforded 50 mg (7.5%) of **4a**, mp 160—162 °C (lit,[7] mp 162—163 °C).

Found: C, 70.33; H, 8.92%. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

*Reaction of **1b** with AcONa.* A mixture of 0.8 g (2.9 mmol) of **1b** and 0.25 g (3.0 mmol) of AcONa in 50 ml of THF was refluxed for 4 hr. The reaction mixture was worked up as described above and separated into two fractions. From the neutral fraction, an oil was obtained after evaporation of the ether. Distillation of the oil gave 0.17 g (35%) of 2-butyl-4,4-dimethyl-2-cyclopenten-1-one (**2b**); bp 65—70 °C/3 mmHg. IR (film): 1730 (C=O) and 1630 cm^{-1} (C=C). NMR (CCl_4): δ 1.20 (s, 6H, two CH_3's), 0.7—2.3 (m, 9H, $-CH_2CH_2CH_2CH_3$), 2.16 (s, 2H, $-CO\mathbf{CH_2}C(CH_3)_2-$), and 6.97 (m, 1H, >C=C**H**–). Mass spectrum: *m/e* 166 (M^+), 151, 138, and 109.

Found: C, 79.41; H, 10.76%. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91%.

The oily material obtained from the Na_2CO_3-soluble fraction was triturated with ice-water. The solid thus precipitated was separated into 0.03 g (5.3%) of **4b**, mp 152—153 °C (lit,[7] mp 155 °C) and 0.09 g (15%) of 2-butyl-5,5-dimethyl-3-oxo-1-cyclopentene-1-carboxylic acid (**3b**) by fractional recrystallization from benzene–CCl_4 (1: 3). An analytical sample of **3b** was prepared by recrystallization from $CHCl_3$; mp 159—162 °C. Mass spectrum; *m/e* 210 (M^+), 182, 166, 153.

Found: C, 68.33; H, 8.98%. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63%.

*Reaction of **1a** with EtONa.* A suspension of 1.0 g (4.3 mmol) of **1a** and 0.58 g (8.6 mmol) of EtONa in 100 ml of dry ether was heated under reflux for 5 hr. The reaction mixture was poured into 50 ml of water and neutralized with 1 M HCl, the ether layer then being separated. The aqueous layer was further extracted twice with 30 ml portions of ether. The ether solutions were combined, washed with 5% Na_2CO_3, dried over Na_2SO_4, and the ether was evaporated. The residual oil was distilled to give 0.47 g (64%) of ethyl 3,3-dimethyl-5-oxoheptanoate (**5a**); bp 73—75 °C/1 mmHg. IR (film): 1735 (sh) and 1730 cm^{-1} (C=O). NMR ($CDCl_3$): δ 1.13 (s, 6H, $(CH_3)_2C-$), 1.20 (t, J=6.0 Hz, 3H, $-COCH_2-\mathbf{CH_3}$), 1.25 (t, J=7.0 Hz, 3H, $-COOCH_2\mathbf{CH_3}$), 1.90 (s, 2H, **$-CH_2-$**), 2.40 (s, 2H, **$-CH_2-$**), 4.12 (q, J=6.0 Hz, 2H, $-CO\mathbf{CH_2}-CH_3$), and 4.20 (q, J=7.0 Hz, 2H, $-COO\mathbf{CH_2}CH_3$). Mass spectrum: *m/e* 200 (M^+), 172, 156, 146, 130, 87, 83, 43, and 29.

Found: C, 65.55; H, 9.82%. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07%.

Vpc analysis of the residual oil indicated that the oil contained 30 mg (5.6%) of 2,4,4-trimethyl-2-cyclopenten-1-one (**2a**). The aqueous Na_2CO_3 solution was neutralized with 1 M HCl, and extracted with ether. The ether extract was dried over Na_2SO_4 and evaporated. The residue was recrystallized from $CHCl_3$ to give 60 mg (9%) of **4a**.

*Reaction of **1a** with t-BuONa.* A mixture of 0.8 g (3.4 mmol) of **1a** with 0.4 g (3.7 mmol) of *t*-BuONa in 50 ml of anhydrous THF was heated under reflux for 5 hr. The reaction mixture was poured into 40 ml of water, neutralized with 1 M HCl and then extracted with two 30 ml portions of ether. The ether extracts were washed with 5% Na_2CO_3, dried and evaporated to leave a tarry material which could not be purified. However, vpc analysis indicated that the tar contained 50 mg (12%) of **2a**. Work-up of the aqueous Na_2CO_3 solution gave 0.18 g (34%) of **4a**.

*Reaction of **1a** with AcOAg.* A mixture of 1.0 g (4.3 mmol) of **1a** and 0.75 g (4.5 mmol) of AcOAg in 40 ml of THF was refluxed with stirring for 5 hr. The reaction mixture was separated into two fractions, *i.e.*, neutral and Na_2CO_3 soluble fractions, by a method similar to that described above. Fractional distillation of the oil obtained from the neutral fraction gave first 90 mg (17%) of **2a**. Trituration of the residue of this distillation gave the solid, which upon fractional recrystallizations from hexane–CCl_4 (5: 1) yielded 0.2 g (20% of unchanged **1a** and 0.06 g (5.3%) of the dimer (**6**).[1] Compound **6** melted at 168—169 °C. IR(KBr): 1725, 1710, 1635, and 1610 cm^{-1}. NMR ($CDCl_3$): δ 1.00—1.17 (m, 12H, four CH_3's), 1.60 (s, 3H, $CH_3C(-O-)$), 1.75 (t, J=2 Hz, 3H, **CH_3**–C=C–CH_2-), 2.04 (q, J=2 Hz, 2H, **$-CH_2-$**C=C–CH_3), 2.23 (s, 2H, $-C=C(CH_3)CO\mathbf{CH_2}-$), and 2.81 (m, 4H, two of $-CO\mathbf{CH_2}C(CH_3)_2-$). Mass spectrum: *m/e* 153 (M—153, 30%), 151 (30), 136 (15), 125 (10), 109 (20), 98 (50), and 83 (100).

Found: C, 70.34; H, 8.52%. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55%.

Work-up of the Na_2CO_3 soluble fraction gave 0.07 g (10%) of **3a** and 0.05 g (7.5%) of **4a**.

When the reaction of 1.0 g (4.3 mmol) of **1a** with 0.75 g (4.5 mmol) of AcOAg was carried out for 18 hr, 0.1 g (19%) of **2a**, 0.02 g (3%) of **3a**, 0.27 g (22%) of **6** and 0.06 g (9%) of **4a** were isolated.

Hydrolysis of **6**. A solution of 0.1 g (0.3 mmol) of **6** in 30 ml of dioxane–water mixture (1: 1) containing 6 M HCl was heated at 80 °C for 3 hr, and then evaporated to dryness under reduced pressure. Recrystallization of the residue from $CHCl_3$ gave 0.09 g (90%) of **4a**.

2,2-Dibromodimedone (7). This compound was prepared by the bromination of dimedone with two equivalents of Br_2 in 77% yield; mp 144—145 °C, (lit,[8] mp 144—146 °C). IR(KBr): 1720 and 1730 cm^{-1}. NMR ($CDCl_3$): 1.05 (s, 6H), and 3.05 (s, 4H).

Found: C, 32.22; H, 3.45%. Calcd for $C_8H_{10}O_2Br_2$; C, 32.25; H, 3.38%.

Reaction of 7 with AcONa. A mixture of 1.5 g (5 mmol) of **7** and 0.45 g (5.5 mmol) of anhydrous AcONa in 60 ml of THF was stirred under reflux for 4 hr. The reaction mixture was separated into two fractions. An oily material obtained from the neutral fraction was chromatographed on silica-gel with hexane–CCl_4 (5: 1) to give 0.33 g (25%) of 2,3-dibromo-4,4-dimethyl-2-cyclopenten-1-one (**8**). An analytical sample of **8** was obtained by recrystallization from hexane; mp 85—86 °C. IR(KBr): 1702 (C=O), and 1570 cm^{-1} (C=C). NMR (CCl_4); δ 1.50 (s, 6H, two CH_3's at the 4-position) and 2.70 (s, 2H, $-CO\mathbf{CH_2}C(CH_3)_2-$). Mass spectrum: *m/e* 270, 268, 266 (1: 2: 1); 255, 253, 251 (1: 2: 1); 227, 225, 223 (1: 2: 1); 189, 187 (1: 1); 161, 159 (1: 1); 133, 131, (1: 1).

Found: C, 31.28; H, 2.98%. Calcd for $C_7H_8OBr_2$; C, 31.38; H, 3.01%.

Another oily material obtained from the Na_2CO_3 soluble fraction was partly solidified on being left to stand overnight in a refrigerator. The solid was separated by filtration and then recrystallized from CCl_4–$CHCl_3$ (2: 1) to give 0.35 g (32%) of **10**: mp 169—172 °C (lit,[8] mp 175—176 °C). IR (KBr): 1620 cm^{-1} (C=O).

Found: C, 43.62; H, 5.13%. Calcd for $C_8H_{11}O_2Br$: C, 43.86; H, 5.06%.

A mixture-melting point test of **10** with its authentic sample showed no depression. The filtrate was chromatographed on silica-gel with $CHCl_3$–CCl_4 (3: 1) to give 0.19 g (16%) of 2-bromo-5,5-dimethylcyclohexane-1,3,4-trione (**9**); mp 188—190 °C. IR(KBr): 3200, 1690, 1665, 1650, and 1620 cm^{-1}. NMR (DMSO-d_6): δ 1.16 (s, 6H, two CH_3's at the 5-position), 2.82 (s, 2H, $-CO\mathbf{CH_2}C(CH_3)_2-$) and 6.02—6.25 (broad s, 1H, $-CO-\mathbf{CH}Br-CO-$). Mass spectrum: *m/e* 234, 232 (1: 1), and 220, 218 (1: 1).

Found: C, 41.20; H, 3.66%. Calcd for $C_8H_9O_3Br$: C, 41.23; H, 3.89%.

Reaction of 7 with Na_2CO_3 and with C_2H_5COONa. The reactions were carried out under conditions similar to those described above. The isolated products are given Table 1.

Reaction of 7 with EtONa. A mixture of 1.5 g (5.0 mmol) of **7** and 0.68 g (10 mmol) of EtONa in 60 ml of dry ether was stirred at reflux temperature for 5 hr. The reaction mixture was separated into two fractions, *i.e.*, neutral and Na_2CO_3-soluble fractions. An oil obtained from the neutral fraction was distilled under reduced pressure to give 0.41 g (38%) of diethyl 3,3-dimethylglutarate (**11**); bp 82—84 °C/3 mmHg. IR (film); 1735 cm^{-1} (C=O). NMR (CCl_4): δ 1.08 (s, 6H, two CH_3's at the 3-position), 1.24 (t, J=7.0 Hz, 6H, two of $COOCH_2\mathbf{CH_3}$), 2.35 (s, 4H, CH_2's at the 2- and 4-positions), 4.12 (q, J=7.0 Hz, 4H, two of $COO\mathbf{CH_2}CH_3$).

Found: C, 61.37; H, 9.06%. Calcd for $C_{11}H_{20}O_4$: C, 61.11; H, 9.32%.

The retention time of **11** in vpc was the same as that of the authentic sample.[9] A solid obtained from the Na_2CO_3-soluble fraction was recrystallized from CCl_4–$CHCl_3$ (2: 1) to give 0.38 g (35%) of 2-bromodimedone (**10**).

Reaction of 7 with AcOAg. A mixture of 1.5 g (5 mmol) of **7** and 0.84 g (5 mmol) of AcOAg in 50 ml of THF was stirred at reflux temperature for 5 hr. The reaction mixture was separated into two fractions. An oily material obtained from the neutral fraction was chromatographed on silica-gel with CCl_4 to give 0.23 g (24%) of 2-bromo-4,4-dimethyl-2-cyclopenten-1-one (**12**), which upon recrystallization from hexane showed mp 67—68 °C. IR(KBr): 1710 (C–O) and 1585 cm^{-1}. NMR(CCl_4): δ 1.26 (s, 6H, two CH_3's at the 4-position), 2.27 (s, 2H, $-CO\mathbf{CH_2}C(CH_3)_2-$), and 7.42 (s, 1H, $-CBr=\mathbf{CH}-$). Mass spectrum: *m/e* 190, 188 (1: 1), 175, 173 (1: 1); 147, 145 (1: 1); 110.

Found: C, 44.43; H, 4.51%. Calcd for C_7H_9OBr: C, 44.47; H, 4.80%.

From the Na_2CO_3-soluble fraction, 0.45 g (41%) of **10** was obtained.

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