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Synthesis of 1,3-Dioxin-4-one Derivatives

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A facile and general synthesis of 2,2-dimethyl-1,3-dioxin-4-one derivatives (**1**) is reported. Treatment of β-keto acids with a mixture of acetone, acetic anhydride, and conc. sulfuric acid or with a mixture of isopropenyl acetate and conc. sulfuric acid gave 2,2-dimethyl-1,3-dioxin-4-ones (**1**). Similar treatment of *tert*-butyl esters of β-keto acids also gave **1**.

Keywords——2,2-dimethyl-1,3-dioxin-4-one derivative; diketene–acetone adduct; diketene; acylketene; β-keto acid; β-keto ester

2,2,6-Trimethyl-1,3-dioxin-4-one, so-called diketene–acetone adduct (**1a**), is easily prepared from diketene and acetone in the presence of an acidic catalyst.[1] On heating, the adduct usually shows behavior similar to that of diketene itself.[2] For instance, the adduct reacts with compounds having a C=N or C≡N bond to produce 1,3-oxazin-4-ones,[3] and with 1,3-dipoles such as isoquinolinium methylides to produce pyrrole derivatives.[4] The adduct also produces acetoacetyl derivatives on heating with alcohols, amines,[1] and amides.[5]

Such diketene-like reactivity of the adduct can be rationalized in terms of thermal fragmentation of the adduct to an acetylketene intermediate (**2a**).[3a] We recently obtained evidence that strongly supports the formation of the acetylketene intermediate (**2a**) in the reaction of the adduct.[3c]

Thus, 5- and 6-substituted 1,3-dioxin-4-ones, by analogy with adduct **1a**, may generate acylketenes **2**, which can be regarded as equivalent to mixed diketenes **3**. In the literature such mixed diketenes **3** are not easily accessible.[6] Though several references are available concerning synthesis of 1,3-dioxin-4-ones (**1**), most of the previous methods utilize 1,4-cycloaddition of ketones to acylketenes (**2**) prepared from acid halides,[7a,b] furanones,[7c,d] or diazoketones.[7e]

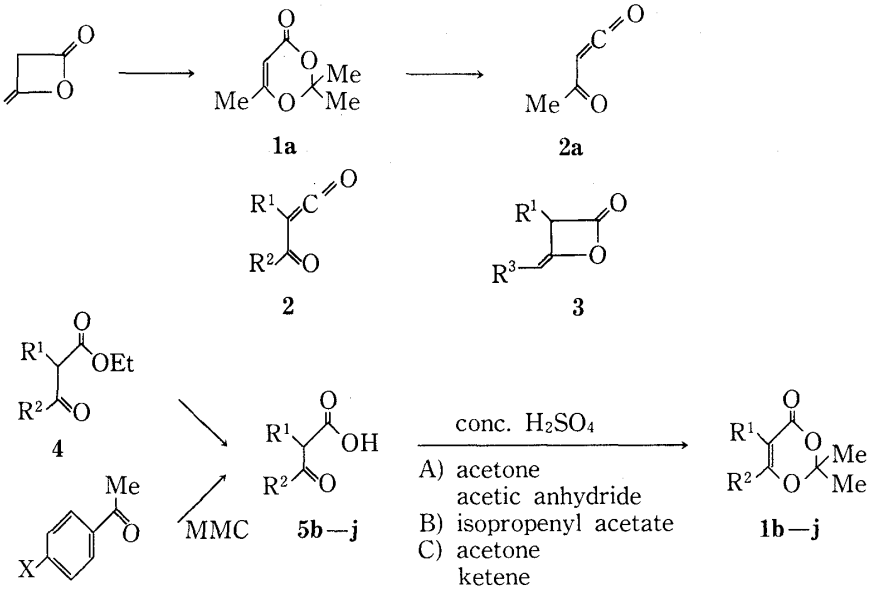
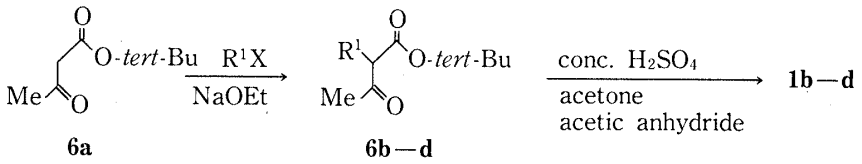


Chart 1

TABLE I. Synthesis of 2,2-Dimethyl-1,3-dioxin-4-ones (**1b—j**) from β-Keto Acids (**5b—j**)

Compd. No.	Substituent		Yield (%)	
	R^1	R^2	Method A	Method B
1b	Me	Me	65	55
1c	Et	Me	68	77
1d	$PhCH_2$	Me	68	63
1e	Ph	Me	89	74
1f	$-(CH_2)_4-$		77	62
1g	Me	Ph	70	82
1h	H	Ph	59	74
1i	H	*p*-MeOPh	47	50
1j	H	*p*-No_2Ph	48	53



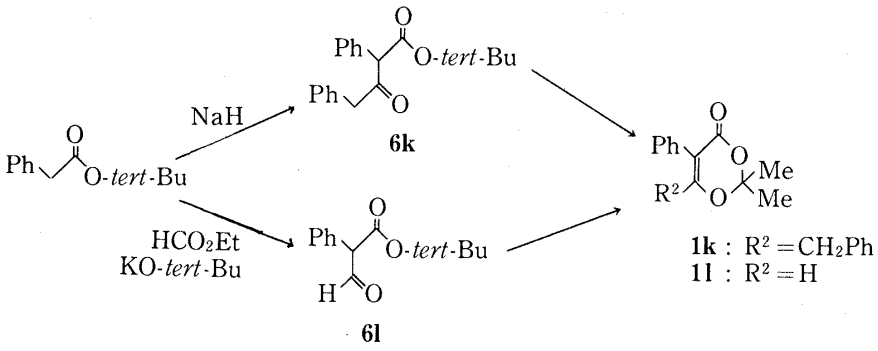


Chart 2

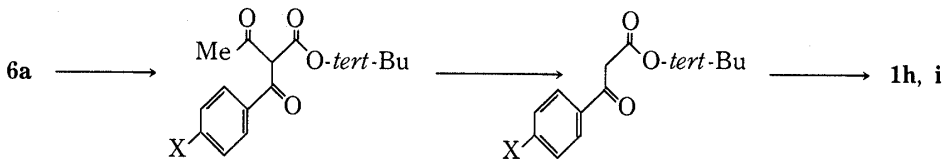


Chart 3

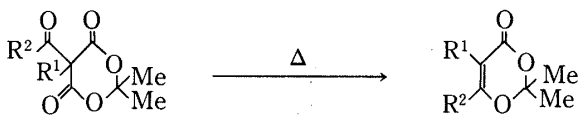


Chart 4

We now report a facile and general synthesis of 1,3-dioxin-4-ones using β-keto acid derivatives.

Acetoacetic acids **5b—e**, 2-oxocyclohexanecarboxylic acid **5f**, and benzoylacetic acids **5g, h** were prepared in good yields by hydrolysis of the corresponding ethyl esters according to the literature. By applying Stiles's method,[8] *p*-anisoyl- and *p*-nitrobenzoylacetic acids (**5i, j**) were prepared by carboxylation of acetophenones with magnesium methyl carbonate (MMC).

Treatment of these acids with a mixture of acetone, acetic anhydride, and a catalytic amount of conc. sulfuric acid produced 1,3-dioxin-4-ones **1b—j** in good yields (method A). Treatment of the acids **5b—j** with a mixture of isopropenyl acetate and conc. sulfuric acid also produced 1,3-dioxin-4-ones **1b—j** (method B). The results are summarized in Table I.

When ketene was used in place of acetic anhydride or isopropenyl acetate, the acid **5h** gave **1h** in 62% yield (method C). Among these methods, method A seems to be most convenient in terms of the procedure, yield, and generality.

Use of *tert*-butyl esters of β-keto acids instead of ethyl esters eliminated the isolation of the acids, resulting in direct formation of 1,3-dioxin-4-ones. *tert*-Butyl 2-alkylacetoacetates **6b—d** were readily prepared from *tert*-butyl acetoacetate (**6a**). Treatment of *tert*-butyl esters **6b—d** with a mixture of acetone, acetic anhydride, and one equivalent of conc. sulfuric acid afforded the dioxinones **1b—d** in good yields. *tert*-Butyl 2,4-diphenylacetoacetate (**6k**) and 2-formylphenylacetate (**6l**) likewise cyclized to 1,3-dioxin-4-ones **1k, l**, respectively.

tert-Butyl benzoylacetate (**6h**) has been synthesized from *tert*-butyl acetate in a low yield (25%).[9] We examined an alternative method based on the procedure given for ethyl benzoylacetates.[10] Thus, *tert*-butyl acetoacetate (**6a**) was treated with benzoyl chloride in the presence of potassium *tert*-butoxide to give the diketo ester **7h** in a good yield. However, deacetylation of crude **7h** afforded **6h** in a low yield (27% from **6a**). *tert*-Butyl *p*-anisoylacetate (**6i**) was

TABLE II. Physical, Analytical, and Spectral Data for 2,2-Dimethyl-1,3-dioxin 4-ones

Compd. No.	mp (°C) or bp (°C/mmHg)	Appearance (recrystn. solvent)[a]	Formula	Analysis (%) Calcd (Found) C	H	IR ($CHCl_3$) cm^{-1}	NMR ($CDCl_3$) δ 2-Me	R^1	R^2
1b	70/3	Oil	$C_8H_{12}O_3$	61.52 (61.24)	7.75 (7.79)	1725 1622	1.60	1.75 (3H, s)	1.94 (3H, s)
1c	76/3	Oil	$C_9H_{14}O_3$	63.51 (63.22)	8.29 (8.16)	1709 1642	1.62	1.03 (3H, t, J=7 Hz) 2.23 (2H, q, J=7 Hz)	1.95 (3H, s)
1d	43—44	Prisms (A)	$C_{14}H_{16}O_3$	72.39 (72.09)	6.94 (7.11)	1712 1640	1.63	3.63 (2H, s) 7.22 (5H, s)	1.99 (3H, s)
1e	66—67	Prisms (B)	$C_{13}H_{14}O_3$	71.54 (71.26)	6.47 (6.32)	1718 1630	1.76	7.30 (5H, s)	1.92 (3H, s)
1f	36—37	Prisms (C)	$C_{10}H_{14}O_3$	65.91 (65.98)	7.74 (7.82)	1716 1650	1.66	1.65 (4H, m),	2.22 (4H, m)
1g	86—87	Prisms (A)	$C_{13}H_{14}O_3$	71.54 (71.74)	6.47 (6.56)	1710 1630	1.78	2.00 (3H, s)	7.48 (5H, s)
1h	62—63	Needles (B)	$C_{12}H_{12}O_3$	70.57 (70.47)	5.79 (5.79)	1717 1622	1.80	5.88 (1H, s)	7.85 (5H, s)
1i	75—76	Leaves (D)	$C_{13}H_{14}O_4$	66.65 (66.45)	6.02 (5.86)	1710 1610	1.79	5.79 (1H, s)	3.87 (3H, s) 6.83 (2H, d, J=13 Hz) 7.66 (2H, d, J=13 Hz)
1j	142 (dec.)	Needles (E)	$C_{12}H_{11}NO_5$	57.83 (57.83)	4.45[b] 4.27)	1720 1620	1.85	6.04 (1H, s)	7.88 (2H, d, J=13 Hz) 8.36 (2H, d, J=13 Hz)
1k	82—83	Needles (C)	$C_{19}H_{18}O_3$	77.53 (77.78)	6.16 6.10)	1720 1630	1.62	7.15 (5H, s)	3.48 (2H, s) 7.25 (5H, m)
1l	38—39	Prisms (C)	$C_{12}H_{12}O_3$	70.57 (70.32)	5.92 5.96)	1722 1622	1.70	7.30 (5H, m)	7.17 (1H, s)
1m	65/1	Oil	$C_6H_8O_3$[c]			1725 1622	1.70	5.30 (1H, d, J=9 Hz)	7.07 (1H, d, J=9 Hz)

a) A, hexane; B, hexane-ether; C, pentane; D, ether; E, ethyl acetate.
b) Calcd: N, 5.62; Found: N, 5.43.
c) Determined by high resolution mass spectrometry. Found: 128.0483; Calcd for $C_6H_8O_3$ (M^+): 128.0473.

similarly prepared in 37% yield. Cyclization of the esters **6h** and **6i** gave 1,3-dioxin-4-ones **1h** and **1i** in 52 and 40% yields, respectively.

The cyclization of *tert*-butyl esters presumably proceeds through the keto acid **5**, since *tert*-butyl esters are easily converted to free acids under acidic conditions. Ethyl esters such as ethyl acetoacetate and benzoylacetate did not cyclize directly to 1,3-dioxin-4-ones under the same conditions.

Iwataki *et al.* have prepared compound **1a** and the 6-ethyl analogue (**1**: R^1=H, R^2=Et) by heating of acetyl Meldrum's acid (**8a**: R^1=H, R^2=Me) and the propionyl analogue (**8**: R^1=H, R^2=Et).[11] Applying this procedure, the formyl compound **8m** (R^1=R^2=H) was heated without solvent to give a resinous product. However, heating of compound **8m** in a mixture of toluene and acetone gave 2,2-dimethyl-1,3-dioxin-4-one (**1m**) in 31% yield. Acetylation of methyl Meldrum's acid afforded 5-acetyl-2,2,5-trimethyl-1,3-dioxane-4,6-dione (**8b**: R^1=R^2=Me). This compound is relatively stable, and the thermal conversion had to be conducted in a sealed tube at 185°C to give **1b** in low yield.

The physical, analytical, and spectral data for 1,3-dioxin-4-ones **1b**—**m** are summarized in Table II. It should be mentioned that the mass spectra of all dioxinones showed the fragment ion peak $(M-58)^+$, which corresponds to the ionized acylketene. This fragmentation resembles the thermal fragmentation of **1a**.

The results of this investigation indicate that the cyclization of β-keto acid derivatives with acetone is a very useful method for preparing a variety of 2,2-dimethyl-1,3-dioxin-4-ones. Thermal reactions of compounds **1b**—**m** with 1,2-, 1,3-, and 1,4-dipoles are under investigation.

Experimental

All melting and boiling points are uncorrected. Infrared (IR) spectra were measured with a JASCO A-102 spectrometer. Nuclear magnetic resonance (NMR) spectra were measured on a JEOL JNM-PMX 60 spectrometer and are reported as δ values (ppm) relative to tetramethylsilane as an internal standard. Mass spectra (MS) were obtained on a Hitachi M-52G mass spectrometer.

General Procedure for Preparation of β-Keto Acids 5b—h——Compounds **5b**,[12] **5c**,[13] **5d**,[12] **5f**,[14] **5g**,[15] and **5h**[16] were prepared from the ethyl esters by slight modifications of the reported procedures. A mixture of a β-keto ester (0.1 mol) and 0.5 N aq. sodium hydroxide (200 ml) was stirred under ice-cooling for 3 h, and then left to stand at room temperature for 12 h. The reaction mixture was washed with ether and acidified with conc. hydrochloric acid under ice-cooling.

The precipitated acids (**5f—h**) were collected by suction, washed with water and then with carbon tetrachloride, and dried. The oily acids (**5b—d**) were extracted with ether from the acidified solution. The ether solution was washed with brine and dried over anhydrous magnesium sulfate. Removal of the ether *in vacuo* at room temperature gave the acids **5b—d** as oily substances.[17] 2-Phenylacetoacetic acid (**5e**) was prepared according to the literature.[18]

***p*-Anisoylacetic Acid (5i)**——*p*-Methoxyacetophenone (3.0 g, 20 mmol) was heated with a 2 M solution of magnesium methyl carbonate[9] in dimethylformamide (40 ml, 80 mmol) at 110—120°C for 1 h. The reaction mixture was poured onto crushed ice, and acidified with conc. hydrochloric acid under ice-cooling. The solution was cooled at −10°C for 1 h. The separated crystals were collected by suction, washed with water and dissolved in 5% sodium carbonate. The solution was filtered and the filtrate was acidified with dil. hydrochloric acid. Separated crystals were collected by suction, washed with water, and dried to give **5i** as fine needles of mp 85—86°C (dec.) (lit.[19] mp 80°C (dec.)). Yield, 1.67 g (43%).

***p*-Nitrobenzoylacetic Acid (5j)**——*p*-Nitroacetophenone (3.30 g, 20 mmol) was treated in the same manner as described above, giving **5j** as fine prisms of mp 130°C (dec.) (lit.[20] mp 135°C (dec.)). Yield, 2.2 g (53%).

General Procedure for Preparation of 2,2-Dimethyl-1,3-dioxin-4-ones (1b—j) from Acids 5b—j. Method A——Conc. sulfuric acid (0.01 mol) was added dropwise to a mixture of one of **5b—j** (0.05 mol), acetone (0.1 mol), and acetic anhydride (0.1 mol) with stirring below 5°C. The mixture was stirred under ice-cooling for 3 h, during which time crystalline **5** dissolved. After being kept in a refrigerator (*ca.* 0°C) for 12 h, the mixture was poured into 10% sodium carbonate solution (120 ml) under ice-cooling. The mixture was stirred at room temperature for 30 min to give the corresponding product.

Separated crystals were collected by suction, washed with water, dried, and recrystallized to give **1d—h**. Oily products **1b, c** were extracted with ether. The ether solution was washed with water, dried over magnesium sulfate and concentrated. Distillation under reduced pressure gave **1b, c**.

Method B——Conc. sulfuric acid (0.01 mol) was added dropwise to a mixture of **5** (0.05 mol) and isopropenyl acetate (0.1 mol) with stirring below 5°C. The mixture was stirred under ice-cooling for 3 h and then kept in a refrigerator for 12 h. The reaction mixture was worked up in the same manner as in method A, giving the corresponding **1**. Yields are shown in Table I. Physical, analytical, and spectral data are shown in Table II.

Method C——Conc. sulfuric acid (380 mg, 4 mmol) was added to a mixture of benzoylacetic acid (**5h**) (1.64 g, 10 mmol) and acetone (2.32 g, 40 mmol) under ice-cooling. Ketene (40 mmol) was introduced into the solution with stirring under ice-cooling. The mixture was kept in a refrigerator for 12 h, then worked up in the same manner as in method A, giving **1h**. Yield, 1.26 g (62%).

***tert*-Butyl 2,4-Diphenylacetoacetate (6k)**——A mixture of *tert*-butyl phenylacetate[21] (3.84 g) and sodium hydride (460 mg) was heated at 90°C with stirring for 2 h. The mixture was neutralized with dil. acetic acid, and precipitated crystals were collected by suction, washed with water, and dried. Recrystallization from pentane gave needles of mp 81—82°C. Yield, 1.9 g (61%). *Anal.* Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.12; H, 7.18. IR ($CHCl_3$): 1735, 1710 cm^{-1}. NMR (CCl_4) δ: 1.40 (9H, s), 3.62 (2H, s), 4.53 (1H, s), 6.90—7.40 (10H, m) (keto form); 1.30 (9H, s), 3.34 (2H, s), 6.90—7.40 (10H, m), 13.15 (1H, s) (enol form) (keto : enol=1 : 1).

***tert*-Butyl 2-Formylphenylacetate (6l)**——Ethyl formate (0.81 g) was added dropwise to a stirred and ice-cooled mixture of *tert*-butyl phenylacetate (1.92 g), potassium *tert*-butoxide (2.24 g), and dry ether (30 ml). After being stirred for 1 h under ice-cooling, the reaction mixture was neutralized with dil. acetic acid and extracted with ether. The ether solution was washed with water and dried over magnesium sulfate. Removal of the solvent *in vacuo* gave an oily substance, which was subjected to silica gel column chromatography. Elution with hexane–ethyl acetate (20 : 1) gave **6l** as prisms (from pentane) of mp 55—56°C. Yield, 1.02 g (46%). *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.82; H, 7.26. IR ($CHCl_3$): 1650 cm^{-1}. NMR (CCl_4) δ: 1.50 (9H, s), 7.17 (5H, s), 7.17 (1H, d, J=13 Hz), 12.14 (1H, d, J=13 Hz) (enol form).

***tert*-Butyl Benzoylacetate (6h)**——*tert*-Butyl acetoacetate (**6a**, 6.32 g) was added dropwise to a mixture of potassium *tert*-butoxide (9.88 g) and dry ether with stirring under ice-cooling. The mixture was stirred at room temperature for 30 min. Benzoyl chloride (6.18 g) was added dropwise to the solution at *ca.* 0°C, and stirring was continued at room temperature for 3 h. The mixture was acidified with 10% hydrochloric acid under ice-cooling and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated to give crude *tert*-butyl 2-benzoylacetoacetate (**7h**) as an oil. Yield, 12 g. Crude **7h** (12 g) was stirred vigorously with a mixture of ammonium chloride (10.24 g), 28% ammonia (9.6 ml), and water (48 ml) at 42°C for 20 min. The mixture was extracted with ether. The ether layer was washed with water, dried over magnesium sulfate and concentrated. Distillation of the residue gave **6h** as an oil of bp 89—93°C (0.1 mmHg) (lit.[9] bp 95°C (0.2 mmHg)). Yield, 5.41 g (27% from compound **6a**).

***tert*-Butyl *p*-Anisoylacetate (6i)**——Following the procedure given for **6h**, compound **6a** (6.32 g) was treated with *p*-anisoyl chloride (7.48 g), giving crude **7i** (12 g) as an oil. Following the procedure for the preparation of **6h**, crude **7i** was deacetylated to give **6i** (6.4 g) as an oil. Purification by silica gel column chromatography using hexane–ethyl acetate (4 : 1) as an eluent gave **6i** as an oil. Yield, 4.0 g (37% from **6a**). IR ($CHCl_3$): 1730, 1680, 1600 cm^{-1}. NMR (CCl_4) δ: 1.20 (9H, s), 3.70 (2H, s), 3.83 (3H, s), 6.85 (2H, d, J=13 Hz), 7.83 (2H, d, J=13 Hz). Cu salt (recrystallized from ethanol): green needles of mp 205—208°C (dec.). *Anal.* Calcd for $C_{28}H_{36}CuO_8$: C, 59.61; H, 6.43. Found: C, 59.47; H, 6.14.

General Procedure for Preparation of Compound 1 from Compound 6——Conc. sulfuric acid (0.03 mol) was added dropwise to a mixture of **6** (0.03 mol), acetone (0.06 mol), and acetic anhydride (0.09 mol) with stirring below −5°C. The mixture was stirred under ice-cooling for 3 h, and then kept in a refrigerator for 12 h. The reaction mixture was poured into 10% sodium carbonate (120 ml) under ice-cooling. The mixture was worked up as described for method A to give **1b** (71%), **1c** (80%), **1d** (60%), **1h** (52%), **1i** (40%), **1k** (65%), or **1l** (90%). Physical, analytical, and spectral data are listed in Table II.

2,2-Dimethyl-1,3-dioxin-4-one (1m)——A mixture of **8m**[22] (2.58 g), acetone (1.74 g) and xylene (60 ml) was heated under reflux for 30 min. The reaction mixture was subjected to silica gel column chromatography. Elution with hexane–ether (8 : 1) gave **1m** as an oil. Physical, analytical, and spectral data are listed in Table II.

5-Acetyl-2,2,5-trimethyl-1,3-dioxane-4,6-dione (8b)——Acetyl chloride (1.73 g) was added dropwise to a mixture of 2,2,5-trimethyl-1,3-dioxane-4,6-dione[23] (3.16 g), pyridine (3.48 g), and dichloromethane (50 ml) with stirring at −10—−5°C. After being stirred for 1 h at room temperature, the mixture was washed with aq. 5% hydrochloric acid, and then with water. The organic layer was dried over magnesium sulfate and concentrated to dryness *in vacuo*. The residue was recrystallized from ether giving **8b** as prisms of mp 67—69°C. Yield, 3.3 g (83%). *Anal.* Calcd for $C_9H_{12}O_5$: C, 53.99; H, 6.04. Found: C, 53.73; H, 6.16. IR ($CHCl_3$): 1790, 1750 cm^{-1}. NMR ($CDCl_3$) δ: 1.80 (6H, s), 1.90 (3H, s), 2.33 (3H, s).

Conversion of Compound 8b to Compound 1b——Compound **8b** (2 g) and acetone (0.87 g) were heated in a sealed tube at 185°C for 1 h. The reaction mixture was distilled under reduced pressure to give 0.5 g (32%) of **1b**.

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