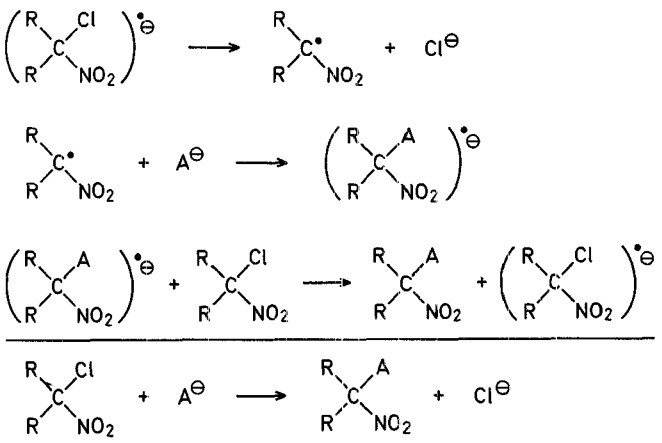
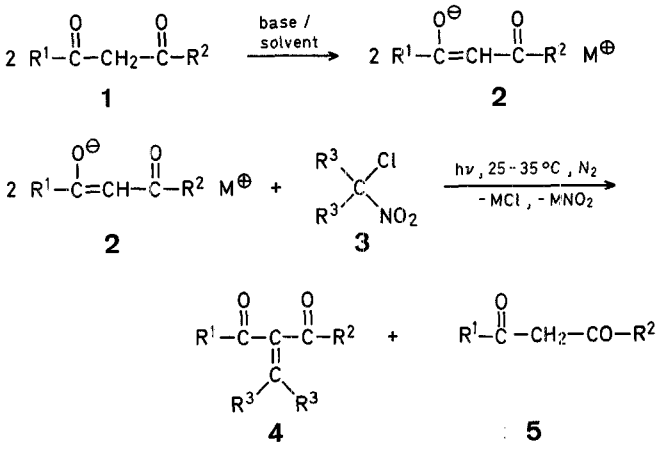


Scheme A

yield of the corresponding isopropylidene derivative[3,4], β-diketones or β-keto esters fail to yield this product. We have, therefore, investigated the conversion of a series of enolates ions **2** to the α-alkylidene derivates **4** via the $S_{RN}1$ process (Scheme **B**).



Scheme B

The conversion of **1** ($R^1 = C_6H_5$, $R^2 = OC_2H_5$) to **4a** using 2-chloro-2-nitropropane (**3**, $R^3 = CH_3$) with a variety of base/solvent systems using a 1:1:1 molar ratio of **1**:**3**:base and sunlamp irradiation was studied. Irradiation is not required, but the reaction occurs more rapidly with irradiation. Even with irradiation, the reactions are completely inhibited by the presence of 5 mol% of di-*t*-butyl nitroxide as expected for the chain process of Scheme **A**. Best results were obtained with sodium hydride/dimethylformamide (50% yield of **4a** after 20 h). Other systems studied include: lithium diisopropylamide/tetrahydrofuran (no reaction after 8 h), sodium methoxide/dimethylformamide (40% yield in 8 h), sodium hydride/dimethyl sulfoxide (39% yield in 8 h), potassium hydride/dimethyl sulfoxide (42% yield in 21 h), and potassium *t*-butoxide/3:1 *t*-butanol/dimethyl sulfoxide (35% yield in 20 h).

The sodium hydride/dimethylformamide system was chosen as the most convenient and further experiments were conducted with a 2-fold excess of the enolate **2** as shown in Scheme **B** (see Table 1).

Three of the products were obtained as keto-enol mixtures (**4c**, **4e**, and **4f**), which were analyzed by ^{1}H-N.M.R. spectrometry (the keto and enol tautomers of 3-isopropylidene-2,4-pentanedione (**4f**) have been previously reported)[5]. In the case of the

α-Alkylidene Derivatives of β-Diketones and β-Keto Esters; 2-Chloro-2-nitropropane as an Acetone Equivalent in Controlled Cross-Aldol-Type Processes[1]

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Geminal halo-nitro-alkanes will participate in the $S_{RN}1$ process (Scheme **A**) with enolate anions of cycloalkanones or ω-alkylacetophenones to yield β-nitro-ketones which readily eliminate nitrous acid to yield α,β-unsaturated ketones[2].

The reactions are sensitive to the nature of the counterion and solvents used to prepare the enolate anion. Although diethyl malonate and acetone can be condensed to give a moderate

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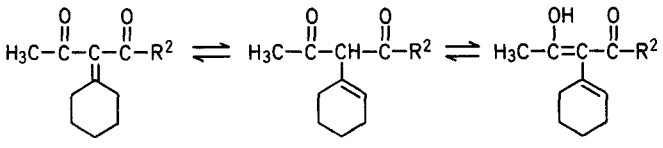
two α-cyclohexylidene derivatives (Scheme C), two keto forms and one enol form were readily distinguished by ^{1}H-N.M.R. spectrometry[6].



$R^2 = C_6H_5$ 23% 40% 37%
$R^2 = OC_2H_5$ 38% 14% 48%

Scheme C

The utility of α-halonitroalkanes as ketone equivalents is increased by their facile synthesis from ketoximes by chlorination in dichloromethane followed by oxidation with nitric acid in cyclohexane in overall yields of 70%.

Ethyl α-Isopropylideneacetoacetate (4b); Typical Procedure:
In a 100 ml flask equipped with a thermometer, dropping funnel, rubber septum for hypodermic injection, and a nitrogen purge, there is placed sodium hydride (1.20 g, 0.05 mol) and dimethylformamide (30 ml). The solution is stirred by a magnetic stirrer while ethyl acetoacetate (2; $R^1 = CH_3$, $R^2 = OC_2H_5$; 6.5 g, 0.05 mol) is added dropwise over a 1 h period followed by an additional 3 h to insure complete conversion to the enolate anion. 2-Chloro-2-nitropropane (3; $R^3 = CH_3$; 2.7 ml, 0.025 mol) is injected from a syringe and the solution stirred for 3 h approximately 6 in from a 275 Watt sunlamp which maintains a reaction temperature of 35 °C. The reaction product is poured into water (200 ml), and the organic products are extracted with hexane (30 ml) followed by benzene (3 × 25 ml). The combined extracts are washed with 5% aqueous sodium hydroxide (75 ml) and dried with magnesium sulfate. Vacuum distillation gives **4b**; yield: 3.25 g (77%); b.p. 100–102 °C/6 torr.

Table 2 lists the properties of the α-alkylidene derivatives and gives references to previous indirect syntheses.

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Table 1. α-Alkylidene β-Diketones or α-Alkylidene β-Ketoesters **4**

Product No.	R^1	R^2	R^3	R^3	Reaction time [h]	Yield [%]	Keto:Enol ratio
4a	C_6H_5	OC_2H_5	CH_3	CH_3	17[a]	74	>20:1
4b	CH_3	OC_2H_5	CH_3	CH_3	3	77 (0)[b]	>20:1
4c	CH_3	OC_2H_5	—$(CH_2)_5$—		3	86	86:14
4d	CH_3	C_6H_5	CH_3	CH_3	8	67	>20:1
4e	CH_3	C_6H_5	—$(CH_2)_5$—		7	56	60:40
4f	CH_3	CH_3	CH_3	CH_3	19	70	55:45
4g[c]	C_6H_5	C_6H_5	CH_3	CH_3	21	65	>20:1

[a] Reaction in the dark.
[b] Reaction in the dark in the presence of 5 mol% of di-*t*-butyl nitroxide.
[c] 2,2-Dinitropropane used instead of 2-chloro-2-nitropropane.

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Table 2. Physical and Spectral Data for Products **4a–g**

Product	b.p. [°C]/torr found	b.p. [°C]/torr reported	I.R. (film) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	Reference for previous preparation
4a	92–95°/0.3	98–100°/0.1[7]	1723; 1676; 1633	1.00 (t, J = 11.7 Hz, 3H); 1.81 (s, 3H); 2.31 (s, 3H); 4.06 (q, J = 11.7 Hz, 2H); 7.5 (m, 3H); 8.0 (m, 2H)	7
4b	101–102°/6	212–218°/760[5]	1727; 1695; 1632	1.30 (t, J = 11.7 Hz, 3H); 1.96 (s, 3H); 2.10 (s, 3H); 2.28 (s, 3H); 4.24 (q, 2H, J = 11.7 Hz)	5,8
4c	73–82°/0.6	—[a]	1750; 1725; 1705; 1640; 1615	Keto form: 1.27 (t, J = 11.8 Hz, 3H); 2.30 (s, 3H); 4.22 (q, J = 11.8 Hz, 2H) Keto form: 1.28 (t, J = 11.8 Hz, 3H); 2.21 (s, 3H); 4.00 (s, 1H); 4.18 (q, J = 11.8 Hz, 2H); 5.7 (m, 1H) Enol form: 1.28 (t, J = 11.8 Hz, 3H); 2.16 (s, 3H); 4.18 (q, J = 11.8 Hz, 2H); 5.5 m (1H); 12.67 (s, 1H)	—
4d	84–86°/0.3	—	1693; 1670; 1610	1.74 (s, 3H); 2.12 (s, 3H); 2.20 (s, 3H); 7.6 (m, 3H); 8.0 (m, 2H)	9
4e	130–136°/0.2	—[b]	3030–3000; 1715; 1680	1.6, 2.0 (2m, $H_{cyclohexyl}$); 2.17–2.27 (br s, CH_3); 4.91 (s, CH); 5.7 (m, H_{vinyl}); 7.4, 7.8 (2m, H_{arom}); 16.84 (s, OH)	—
4f	90–120°/8	85–100°/30[5]	—	Keto form: 1.96 (s, 6H); 2.29 (s, 6H) Enol form: 1.91 (s, 3H); 2.09 (s, 6H); 4.9, 5.2 (2m, 2H); 16.5 (s, 1H)	5
4g	138–142°/0.1 m.p. 76.5–78.0°	—[c]	1650[d]	1.88 (s, 6H); 7.5 (m, 6H); 8.0 (m, 4H)	—

[a] $C_{12}H_{18}O_3$ (210.1) calc. C 68.55 H 8.63; found 68.14 8.84
M.S. (80 eV): m/e = 210.1254 (M^+; calc. 210.1256).
[b] $C_{16}H_{18}O_2$ (242.1) calc. C 79.31 H 7.49; found 79.16 7.55
M.S. (80 eV): m/e = 242.1301 (M^+; calc. 242.1307).
[c] $C_{18}H_{16}O_2$ (264.1) calc. C 81.79 H 6.10; found 82.14 6.15
M.S. (80 eV): m/e = 264.1154 (M^+; calc. 264.1150).
[d] In $CHCl_3$ solution.