Alkylation of Nitrile Anions by Tertiary α-Halo Ketones and Nitriles†

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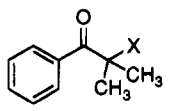
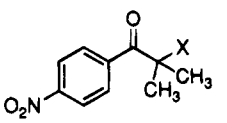
Potassium salts of nitriles bearing carbethoxy, cyano, or phenyl groups at the α carbon [(RR'CCN)K: R' = CO_2Et, CN, Ph] react with tertiary α-halo ketones and nitriles (**1**–**5**) in DMSO or HMPA to provide the alkylated β-keto- or β-cyano-β,β-dialkyl nitriles **6**–**10** in useful yields. $(PhCHCN)^-$ undergoes cyclization with p-$XC_6H_4COCCl(CH_3)_2$ to produce 2(5*H*)-furanone **11**. Reaction of $(Ph_2CCN)^-$ with $PhCOCCl(CH_3)_2$ affords the hydrolyzed ketone **12a** and recovered carbon acid, while the anion undergoes oxidative dimerization to $NCCPh_2CPh_2CN$ with p-$O_2NC_6H_4COCCl(CH_3)_2$ with concomitant formation of the reduced ketone p-$O_2NC_6H_4COCH(CH_3)_2$ and the hydrolyzed ketone **12b**. The alkylations of $[NCC(CH_3)CO_2Et]^-$ and $[NCC(CH_3)CN]^-$ with p-$O_2NC_6H_4COCX(CH_3)_2$ take place by the $S_{RN}1$ process.

The alkylation of resonance stabilized carbanions by tertiary benzyl halides has been intensively studied in connection with the study of $S_{RN}1$ reactions.[1,2] However, examples of the alkylation of these types of carbanions with other classes of tertiary, α-substituted alkyl halides are more scattered in the literature.[3] The diethyl malonate anion can be alkylated with trityl bromides.[4] Alkylation of carbanions with tertiary allylic halides is a rare reaction and is sometimes disfavored relative to an allylic rearrangement;[5a] (α-amino)arylacetonitrile anions and $(CH_3)_2CBrCH{=}CHCO_2Et$ gave mixed unrearranged and rearranged products,[5b] while ethylmalononitrile anion and sterically crowded PhCH=CHCH(*t*-Bu)Cl afforded predominantly the unrearranged product.[5c]

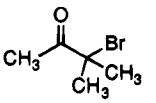
Tertiary α-bromo carboxylic esters, mainly $(CH_3)_2CBrCO_2Et$, have been reported to alkylate anions of malonic esters,[6a] α-cyano carboxylic esters,[6b] and phenylacetonitriles.[6c] The tertiary α-cloro ketones **1a** and **2a** have been reported to alkylate nitroalkane anions by the $S_{RN}1$ process;[7] a single example of the alkylation of a nitrile anion by a tertiary α-halo ketone was described, namely, the alkylation of ethyl cyanoacetate anion by **2a**. Regarding tertiary α-halo nitriles, it is known that **4** can undergo $S_{RN}1$ alkylations with nitroalkane anions.[8] We report here our work on the alkylation of anions of α-cyano esters $[(NCCHCO_2Et)^-$, $[NCC(CH_3)CO_2Et]^-]$, methylmalononitrile $[[NCC(CH_3)CN]^-]$, or phenylacetonitriles $[(PhCHCN)^-, (Ph_2CCN)^-]$ with the tertiary α-halo ketones or nitriles **1**–**5**.



1a: X = Cl
1b: X = Br



2a: X = Cl
2b: X = Br



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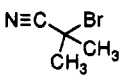

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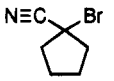

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Results and Discussion

The reactions were accomplished using the potassium salts of the nitriles with DMSO or HMPA as the solvent in which all of the salts were soluble. The reaction conditions and yields for the alkylated β-keto- or β-cyano-β,β-dialkyl nitriles **6**–**10** are shown in Table 1. Photoirradiation was necessary in the reaction of α-chloro-*p*-nitroisobutyrophenone (**2a**) with $[NCC(CH_3)CO_2Et]^-$ to obtain a reasonable yield of the alkylate (**7a**), which supports the occurrence of an $S_{RN}1$ process; only 4% of **7a** was isolated from the unirradiated reaction in DMSO versus 38% with sunlamp irradiation. All other alkylation reactions in Table 1 proceeded under ordinary laboratory light to provide moderate yields of isolated products. We tested the effect on yield of changing the solvent from DMSO to HMPA for two reactions of the aromatic α-halo ketones, i.e., the reaction of α-bromoisobutyrophenone (**1b**) with $(Ph_2CCN)^-$ and the irradiated reaction of **2a**. In both cases the isolated yields of the alkylates were noticeably improved with HMPA. Based upon this, the alkylations of the aliphatic α-bromo

† Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

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(1) For a review on the $S_{RN}1$ process see: Russell, G. A. *Adv. Phys. Org. Chem.* **1987**, *23*, 271–322.

(2) (a) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 725–727. (b) Jacobs, B. D.; Kwon, S.-J.; Field, L. D.; Norris, R. K.; Randles, D.; Wilson, K.; Wright, T. A. *Tetrahedron Lett.* **1985**, *26*, 3495–3498.

(3) The alkylation of resonance stabilized carbanions by nucleophilic displacement reactions is considered in the following reviews, among others: Cope, A. C.; Holmes, H. L.; House, H. O. *Org. React.* **1957**, *9*, 107–331. Kaiser, E. M.; Petty, J. D.; Knutson, P. L. A. *Synthesis* **1977**, 509–550. Arseniyadis, S.; Kyler, K. S.; Watt, D. S. *Org. React.* **1984**, *31*, 1–364. Wardell, J. L. In *The Chemistry of the Functional Groups: The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; Wiley: Chichester, 1987; Vol. 4, pp 1–157. De Kimpe, N.; Verhé, R. In *The Chemistry of the Functional Groups: The Chemistry of α-Haloketones, α-Haloaldehydes and α-Haloimines*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1988; pp 1–496. Braun, M. In *Methoden der Organischen Chemie: Carbanionen*; Hanack, M., Ed.; Thieme: Stuttgart, 1993; pp 853–1138.

(4) Holmberg, G. A. *Acta Acad. Aboensis Math. et Phys.* **1948**, *16*, 1–138 (*Chem. Abstr.* **1951**, *45*, 558).

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(6) (a) Bischoff, C. A.; Mintz, N. *Chem. Ber.* **1890**, *23*, 647–652. (b) Bone, W. A.; Sprankling, C. H. G. *J. Chem. Soc.* **1899**, *75*, 839–864. (c) Salmon-Legagneur, F.; Neveu, C. *Bull. Soc. Chim. Fr.* **1962**, 2130–2136. Eastman, R. H.; Tamaribuchi, K. *J. Org. Chem.* **1965**, *30*, 1671–1673.

(7) Russell, G. A.; Ros, F. *J. Am. Chem. Soc.* **1985**, *107*, 2506–2511.

(8) Ros, F.; de la Rosa, J. *J. Org. Chem.* **1988**, *53*, 2868–2870.

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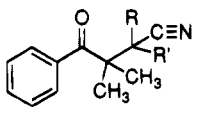
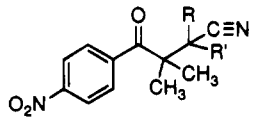
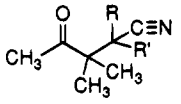
ketone **3** and α-bromo nitriles **4** and **5** were accomplished in this solvent. It is noteworthy that the assayed alkylations with α-bromo ketone **3**, which bears α′ hydrogens, took place favorably over conceivable Favorskii-type rearrangements. Also, the alkylations with tertiary α-bromo nitriles occurred in preference to the possible addition of the anions to the cyano group.[9] Dialkylation products were not found in the assayed alkylations of anions of secondary nitriles [$(NCCHCO_2Et)^-$, $(PhCHCN)^-$], which we ascribe to steric constraints, particularly when the alkylating agent was the more sterically hindered α-halo phenyl ketones **1a,b** rather than α-bromo nitrile **4**.[10] On the other hand, in the reaction of $(PhCHCN)^-$ with **4**, the monoalkylate **9b** underwent partial dehydrocyanation to form $(CH_3)_2C{=}CPhCN$ as a minor product. Olefin-forming dehydrohalogenation in the reaction of tertiary alkyl halides **1**–**5** with nitrile anions was observed only in the reaction of cyclic α-bromo nitrile **5** with $(Ph_2CCN)^-$ (see footnote *j* in Table 1).



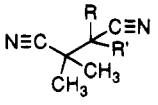
6a: R = H, R' = CO_2Et
6b: R = CH_3, R' = CO_2Et
6c: R = CH_3, R' = CN
6d: R= H, R' =Ph
6e: R = R' = Ph



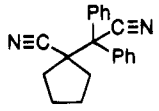
7a: R = CH_3, R' =CO_2Et
7b: R = CH_3, R' = CN



8a: R = CH_3, R' = CO_2Et
8b: R = R' = Ph



9a: R = CH_3, R' = CO_2Et
9b: R = H, R' = Ph
9c: R = R' = Ph



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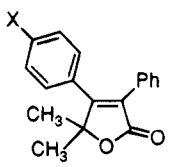
Attempted alkylation of $[NCC(CH_3)CO_2Et]^-$, $(PhCHCN)^-$, and $(Ph_2CCN)^-$ with α-chloroisobutyrophenone (**1a**) failed, unlike alkylation of $(NCCHCO_2Et)^-$ and $[NCC(CH_3)CN]^-$ with the same ketone. The former reactions gave at best very low yields of the products, even with sunlamp irradiation. For instance, $[NCC(CH_3)CO_2Et]^-$ gave <5% of **6b** with or without irradiation. Thus, the substitution of **1a** was preferred for the two latter carbanions, which are more difficult to oxidize[2a,11] and smaller than the others, suggesting that **1a** alkylates them by the S_N2 mechanism rather than by the electron transfer $S_{RN}1$ process. Furthermore, with α-bromoisobutyrophenone (**1b**) as the alkylating agent instead of **1a**, the products of the reaction with $[NCC(CH_3)CO_2Et]^-$, $(PhCHCN)^-$, and $(Ph_2CCN)^-$ were adequately obtained, suggesting that S_N2 reactions took place.

Table 1. Alkylation Reactions of Nitrile Anions with α-Halo Ketones and Nitriles

halo compound	anion	conditions[a]	alkylate, % yield[b]
1a	$(NCCHCO_2Et)^-$	DMSO, rt, 16 h[c]	**6a**, 70
1a	$[NCC(CH_3)CN]^-$	DMSO, rt, 68 h	**6c**, 32[d]
1b	$[NCC(CH_3)CN]^-$	DMSO, rt, 5 h	**6c**, 45
1b	$[NCC(CH_3)CO_2Et]^-$	DMSO, rt, 5 h	**6b**, 54
1b	$(PhCHCN)^-$	HMPA, rt, 1 h	**6d**, 51[e]
1b	$(Ph_2CCN)^-$	DMSO, rt, 1 h	**6e**, 36
		HMPA, rt, 1 h	**6e**, 67
2a	$[NCC(CH_3)CO_2Et]^-$	DMSO, *hν*,[f] 20–40 °C, 5 min	**7a**, 38[g]
		HMPA, *hν*,[f] 20–40 °C, 5 min	**7a**, 66
2a	$[NCC(CH_3)CN]^-$	DMSO, rt, 6 h	**7b**, 62
3	$[NCC(CH_3)CO_2Et]^-$	HMPA, rt, 5 h	**8a**, 88
3	$(Ph_2CCN)^-$	HMPA, 0 °C, 1 h	**8b**, 50
4	$[NCC(CH_3)CO_2Et]^-$	HMPA, rt, 23 h	**9a**, 59
4	$(PhCHCN)^-$	HMPA, 0 °C, 2.5 h[h]	**9b**, 42[i]
4	$(Ph_2CCN)^-$	HMPA, 0 °C, 1 h	**9c**, 66
5	$(Ph_2CCN)^-$	HMPA, 0 °C, 2 h	**10**, 48[j]

[a] Alkylations performed using the nitrile potassium salts (generated *in situ* from the nitriles with 1 equiv of *t*-BuOK), with 1 equiv of halo compound, under N_2, and in ordinary laboratory light, except as noted; reactions were conducted to >80% conversion. [b] Isolated yields of alkylates. [c] With 0.5 equiv of **1a**. [d] 6% of the α-hydroxy ketone **12a** isolated. [e] 8% of the 2(5*H*)-furanone **11a** isolated. [f] *hν* irradiation with a 300-W sunlamp at ca. 15 cm. [g] 21% of the α-hydroxy nitro ketone **12b** isolated; 30% of recovered $NCCH(CH_3)CO_2Et$ (by ^1H NMR). [h] With 0.7 equiv of **4**. [i] 16% of $(CH_3)_2C{=}CPhCN$ (by ^1H NMR). [j] 40% of α-cyclopentenecarbonitrile (by ^1H NMR).

In place of alkylation products, we frequently found products arising from the addition of the nitrile anions to the carbonyl group in the α-chloro ketones (**1a**, **2a**). Thus, $(PhCHCN)^-$ with **1a** afforded 2(5*H*)-furanone **11a**, which crystallized from the acidic aqueous phase resulting from the reaction workup, in 81% yield. Furanone **11b** was likewise obtained from reaction of the anion with



11a: X = H
11b: X = NO_2

α-chloro nitro ketone **2a** in 41% yield. These reactions represent a simple straightforward synthesis of the 2(5*H*)-furanones **11**; known **11a** has been reported from the similar, direct reaction of $(PhCHCO_2)^{2-}$ with α-bromoisobutyrophenone (**1b**), albeit in very low yield.[12] As shown in Scheme 1, the furanones could result from the acidic hydrolysis of cyclic imino esters formed by a Pinner-type intramolecular addition of the alkoxide ion to the cyano group from intermediate cyano alkoxides;

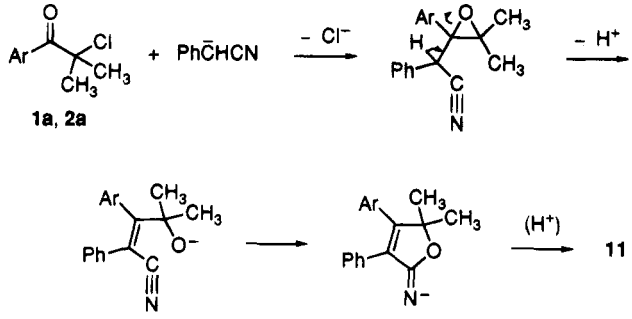
(9) The known β-cyano-β,β-dimethyl nitriles **9a** and **9c** have formerly been prepared by stepwise procedures which do not involve nucleophilic substitution at tertiary alkyl halides. (a) **9a**: Higson, A.; Thorpe, J. F. *J. Chem. Soc.* **1906**, *89*, 1455–1472. (b) **9c**: Schweng, J.; Zbiral, E. *Monatsch. Chem.* **1976**, *107*, 537–546.

(10) Dialkylation of secondary carbanions with alkyl halides is frequently difficult to stop: Kenyon, W. G.; Kaiser, E. M.; Hauser, C. R. *J. Org. Chem.* **1965**, *30*, 4135–4138. We often carried out the alkylations of secondary carbanions using a defect of alkyl halide (see footnotes *c* and *h* in Table 1); these are conditions which favor monoalkylation.

(11) Russell, G. A.; Moye, A. J.; Nagpal, K. *J. Am. Chem. Soc.* **1962**, *84*, 4154–4155. Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035–1037.

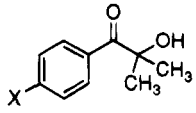
(12) Yandovskii, V. N.; Momchev, M. K. *Dokl. Bolg. Akad. Nauk* **1968**, *21*, 897–900 (*Chem. Abstr.* **1969**, *70*, 28360m). Also, **11a** has been prepared in a stepwise fashion: Blagoev, B.; Novkova, S. *Tetrahedron* **1982**, *38*, 1609–1613.

Scheme 1



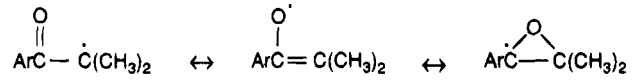
these cyano alkoxides would be formed by a 1,2-shift of the oxygen atom, which is feasible by loss of the acidic hydrogen.[13]

Reaction of $(Ph_2CCN)^-$ with α-chloro ketone **1a** provided only 4% of **6e**; the major isolated reaction product was α-hydroxy ketone **12a** (44%), and it was accompanied by a significant amount of recovered Ph_2CHCN (49%). This suggests the formation of an epoxide analogous to that shown in Scheme 1 for $(PhCHCN)^-$, which would be hydrolyzed during workup. It should be noted that α-hydroxy ketone **12a** and its *p*-nitro derivative **12b** were eventually isolated as minor byproducts in the alkylation reactions shown in Table 1 (*footnotes d and g*).



12a: X = H
12b: X = NO_2

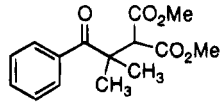
The outcome of the reaction of $(Ph_2CCN)^-$ with α-chloro nitro ketone **2a** was strikingly different. Oxidative dimerization of the anion to tetraphenylsuccinonitrile ($NCCPh_2CPh_2CN$, 83% isolated), concomitant formation of the reduced ketone *p*-nitroisobutyrophenone [p-$O_2NC_6H_4COCH(CH_3)_2$, 42% isolated], and formation of α-hydroxy nitro ketone **12b** (28% isolated), took place. In this particular reaction of an easily oxidized carbanion and a powerful electron acceptor, SET is likely;[14] $Ph_2CCN^\cdot$ generated in this manner could self-couple to the obtained dimer. Furthermore, for the reaction of *p*-nitroisobutyrophenone anion [$[p$-$O_2NC_6H_4COC(CH_3)_2]^-$] with **2a** under the conditions for the reaction between $(Ph_2CCN)^-$ and **2a**, we observed by ^1H NMR spectroscopy a p-$O_2NC_6H_4COCH(CH_3)_2$/**12b** ratio of 0.4:1, which was quite different from the ratio of 1.6:1 for the same products in the reaction of $(Ph_2CCN)^-$. This result does not support the involvement of $[p$-$O_2NC_6H_4COC(CH_3)_2]^-$ in the reaction between $(Ph_2CCN)^-$ and **2a**, which would be formed by Cl^+ transfer from **2a** to the anion. Instead, p-$O_2NC_6H_4COCH(CH_3)_2$ and **12b** could arise from dimerization of the SET-generated α-keto radical (**13**) produced from p-$O_2NC_6H_4COCCl(CH_3)_2^{\bullet-}$ by loss of Cl^-, to either a hydrolyzable peroxide, enol ether, or epoxide.[15] H· transfer to **13** from the solvent (DMSO) could be an



13: Ar = p-$O_2NC_6H_4$

alternative pathway to the reduced ketone. Anions similar to the phenylacetonitrile anion have been shown to dimerize rather than undergo substitution when participating in electron transfer processes with functionally α-substituted alkyl halides.[1] This supports the idea of an electron transfer process for the reaction of $(Ph_2CCN)^-$ with **2a**. Reaction of the anion with α-bromo-*p*-nitroisobutyrophenone (**2b**) produced the same products as with **2a**.

We found it more difficult to alkylate carboxylic ester anions than nitrile anions. Thus, from reaction of $(MeO_2CCHCO_2Me)^-$ with α-bromoisobutyrophenone (**1b**) the alkylation product **14** was isolated in 28% yield, while 64% of **6a** was isolated from the analogous alkylation of



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$(NCCHCO_2Et)^-$. Furthermore, alkylation products were not obtained in the reaction between $(Ph_2CCO_2Me)^-$ and **1b**, or between $[EtO_2CC(CH_3)CO_2Et]^-$ and α-bromoisobutyronitrile (**4**). In the former case we observed elimination to give $PhCOC(CH_3)=CH_2$.

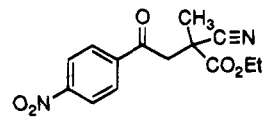
The electron-transfer radical-chain $S_{RN}1$ mechanism is possible for tertiary alkyl halides activated by electron acceptor groups at the α carbon.[1,7,8] We tested this with the aromatic α-halo ketones (**1,2**) by looking at the effect of small proportions of $S_{RN}1$ inhibitors (di-*tert*-butyl nitroxide or *m*-dinitrobenzene) on alkylation. Our results are collected in Table 2. The alkylate yields, determined by ^1H NMR spectroscopy, were considered to be of significant difference when the error of the average was > |10%|. We did not observe the effect of the inhibitors on **1a** and **1b**. As already pointed out, the influence of the nucleophile or nucleofuge on the types of products formed from these α-halo phenyl ketones is better accommodated using the S_N2 mechanism for alkylation; the steric effect of the smaller acetyl or cyano group in **3**–**5** upon substitution should be decreased. In striking contrast to **1**, and strongly supporting the $S_{RN}1$ mechanism, the irradiated reaction of α-chloro-*p*-nitroisobutyrophenone (**2a**) with $[NCC(CH_3)CO_2Et]^-$, as well as with $[NCC(CH_3)CN]^-$, were completely inhibited by $(t\text{-}Bu)_2NO^\cdot$.[16] On the other hand, α-bromo-*p*-nitroisobutyrophenone (**2b**) successfully alkylated $[NCC(CH_3)CO_2Et]^-$ in a reaction that was not well inhibited by the nitroxide. We attribute this to a faster $S_{RN}1$ reaction with a short inhibition period. $[NCC(CH_3)CO_2Et]^-$ did not prove to be as capable a nucleophile for $S_{RN}1$ reactions as the archetypical 2-nitropropane anion. Thus, this nitrile anion, when reacted with α-chloro-*p*-nitroacetophenone, formed alkylation product **15** in 48% (NMR) yield, in a reaction that was totally unaffected by 10 mol % $(t\text{-}Bu)_2NO^\cdot$, indicating an S_N2 mechanism, while the 2-nitropropane anion can be alkylated with the same primary

(13) A related process occurs in the intramolecular cyclization of certain epoxy nitriles, promoted by base, to bicyclic imino esters: Achini, R.; Oppolzer, W. *Tetrahedron Lett.* **1975**, *16*, 369–372.

(14) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807–1814.

(15) Dimerization of **13** to 1,4-diketone, which actually was not found as a reaction product, is not expected, as parent $PhCOC(CH_3)_2^\cdot$ will not behave in this fashion: Kharasch, M. S.; McBay, H. C.; Urry, W. H. *J. Am. Chem. Soc.* **1948**, *70*, 1269–1274.

(16) The total lack of effect of m-$C_6H_4(NO_2)_2$ on the reaction between **2a** and $[NCC(CH_3)CO_2Et]^-$ should be due to an inefficacious electron transfer from the intermediate *p*-nitrophenyl radical anions $[ArCOCCl(CH_3)_2^{\bullet-}$, $ArCOC(CH_3)_2C(CN)(CH_3)CO_2Et^{\bullet-}]$ to the additive.



15

α-chloro ketone clearly by an $S_{RN}1$ mechanism.[7] On the other hand, the greater ability of the α-halo *p*-nitrophenyl ketones (**2**) relative to their unsubstituted phenyl counterparts **1** to participate in $S_{RN}1$ reactions with nitrile anions is supported by an earlier report concerning these α-halo ketones and other classes of anions.[7]

In summary, this work shows that *C*-alkylation of nitrile anions bearing various resonance-stabilizing electron-withdrawing groups at the α carbon can be adequately accomplished with tertiary, α-keto, or α-cyano alkyl halides. The favorable outcome of the alkylation is nevertheless subject to the structural features of the reactants.

Experimental Section

The following starting compounds were prepared by literature procedures: nitriles $NCCH(Me)CO_2Et$[17] and NCCH(Me)CN,[18] and halo compounds **1a**,[19] **2a**,[7] **2b**,[7] **3**[20] (from $MeCOCHMe_2$ with Br_2), **4**[21] (from Me_2CHCN with PBr_5), and **5**[8] [**3**: ^1H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 1.84 (s, 6 H)]. All other chemicals were obtained from commercial sources. *t*-BuOK was frequently checked by titration with standard HCl, being >95%. Solvent DMSO and HMPA were distilled from CaH_2 under vacuum, and were stored over molecular sieves, under N_2, and in the dark. Elemental analyses were performed by Instituto de Química Orgánica General (CSIC).

General Procedure for Alkylation Reactions. The generation of potassium salts of nitriles and their subsequent alkylation were performed in a thorough N_2 atmosphere. To a well stirred solution of *t*-BuOK (1−2 mmol) in the reaction solvent (DMSO or HMPA) was slowly added 1 equiv of nitrile in solution to get a clear solution of nitrile potassium salt and then 1 equiv of halo compound was added neat (by a volumetric microsyringe) or in solution [densities (g/mL): **3**, 1.34; **4**, 1.36; **5**, 1.45]. The total solvent volume was adjusted to make a 0.3 M solution both in nitrile salt and halo compound. Workup was accomplished by dilution with H_2O, extraction with Et_2O, washing with H_2O (thoroughly when HMPA was the reaction solvent), and drying (Na_2SO_4); for the reactions of salts of secondary nitriles [$(NCCHCO_2Et)K$ and (PhCHCN)K] the reaction mixture was diluted with aqueous 1 M HCl. Preparative TLC's or column chromatographies were performed on silica gel, with products separated by TLC being extracted from the adsorbent by Et_2O or $CHCl_3$; the new compounds purified by these methods were routinely recrystallized or Kugelrohr distilled (ca. 0.1 Torr) before elemental analysis.

The experiments in Table 2 with $(t\text{-}Bu)_2NO\cdot$ or $m\text{-}C_6H_4(NO_2)_2$ were carried out adding these compounds together with the α-haloisobutyrophenone in solution. For irradiations was used a 300-W sunlamp positioned at ca. 15 cm from the reaction flask. To control the temperature (±1 °C) several experiments were carried out in a water-jacketed flask along with a thermostat. Unreacted $(t\text{-}Bu)_2NO\cdot$ was removed from the crude reaction mixture under vacuum at 60-80 °C before quantitative ^1H NMR analysis. Absolute ^1H NMR yields were adequately determined with a small proportion of weighed DMF added to the crude mixture.

Carcinogenic HMPA and benzene should be handled with caution.

Ethyl β-Benzoyl-α-cyanoisovalerate (6a). Reaction of $(NCCHCO_2Et)K$ (1.9 mmol) with **1a** (1.0 mmol) in DMSO (3.5 mL, 16 h) followed by TLC (C_6H_6) gave 70% of **6a**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.60 (m, 2 H), 7.45 (m, 3 H), 4.42 (s, 1 H), 4.23 (q, J = 7.1 Hz, 2 H), 1.56 (s, 6 H), 1.29 (t, J = 7.1 Hz, 3 H); IR (neat) 2260, 1748, 1680 cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.47; H, 6.62; N, 5.40. Found: C, 69.60; H, 6.66; N, 5.70.

In the same manner 64% of **6a** (identified by ^1H NMR spectrum) was isolated from reaction of the nitrile salt (3.1 mmol) with α-bromo ketone **1b** (1.6 mmol) in HMPA (5.5 mL, 4 h).

Ethyl β-Benzoyl-α-cyano-α-methylisovalerate (6b). Reaction of $(NCCMeCO_2Et)K$ with **1b** in DMSO (5 h), followed by digestion of the crude product in petroleum ether and recrystallization of the resulting solid in petroleum ether/CH_2Cl_2, gave 54% of **6b**: mp 63−64 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.59 (m, 2 H), 7.45 (m, 3 H), 4.30 (m, 2 H), 1.71 (s, 3 H), 1.63 (s, 3 H), 1.61 (s, 3 H), 1.37 (t, J = 7.1 Hz, 3 H); IR (KBr) 2220, 1738, 1692 cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.30; H, 7.02; N, 5.13. Found: C, 70.10; H, 7.09; N, 5.05.

From reaction of the nitrile salt with α-chloro ketone **1a** in DMSO with sunlamp irradiation [2.5 h, 22% of **1a** recovered (by ^1H NMR)], 1% of **6b** (mp 58−61 °C) was isolated by TLC (C_6H_6).

(α-Benzoylisopropyl)(methyl)malononitrile (6c). Reaction of (NCCMeCN)K with **1a** in DMSO (68 h) followed by TLC (C_6H_6/AcOEt 95:5) gave 32% of **6c**: mp 84−85 °C (from petroleum ether/CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.73 (m, 2 H), 7.54 (m, 1 H), 7.44 (m, 2 H), 1.88 (s, 3 H), 1.70 (s, 6 H); IR (KBr) 2245, 1670 cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.30; H, 6.25; N, 12.38. Found: C, 74.41; H, 6.49; N, 12.45.

By TLC was also isolated, at lower R_f than **6c**, α-hydroxyisobutyrophenone (**12a**) in 6% yield (^1H NMR spectrum in agreement with the literature[7]).

In the same manner 45% of **6c** (mp 84−85 °C) was isolated from reaction of the nitrile salt with α-bromo ketone **1b** in DMSO (5 h).

β-Benzoyl-α-phenylisovaleronitrile (6d). Reaction of (PhCHCN)K with **1b** in HMPA (1 h) followed by column chromatography (hexane/C_6H_6 3:2) gave 51% of **6d**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44 (m, 1 H), 7.35 (m, 9 H), 4.70 (s, 1 H), 1.56 (s, 3 H), 1.30 (s, 3 H); IR (neat) 2225, 1672 cm^{-1}. Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.52; N, 5.32. Found: C, 81.98; H, 6.24; N, 5.60.

From the combined acidic aqueous phases of the workup slowly crystallized 5,5-dimethyl-3,4-diphenyl-2(5*H*)-furanone (**11a**) in 8% yield (mp 156−158 °C, lit.[12] mp 155−156 °C).

β-Benzoyl-α,α-diphenylisovaleronitrile (6e). Reaction of $(Ph_2CCN)K$ with **1b** in DMSO (1 h) followed by TLC (C_6H_6) gave 36% of **6e**: mp 118−119 °C (from hexane/CH_2Cl_2); ^1H NMR ($CDCl_3$, 90 MHz) δ 7.48 (m, 5 H), 7.33 (s, 10 H), 1.60 (s, 6 H); IR (KBr) 2220, 1682 cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO$: C, 84.91; H, 6.25; N, 4.13. Found: C, 85.21; H, 6.57; N, 4.27.

From the reaction in solvent HMPA (1 h) was isolated, in the same manner, 67% of **6e** (mp 116−118 °C).

Ethyl α-Cyano-α-methyl-β-(*p*-nitrobenzoyl)isovalerate (7a) and α-Hydroxy-*p*-nitroisobutyrophenone (12b).[7] $(NCCMeCO_2Et)K$ reacted with **2a** in DMSO with sunlamp irradiation (5 min). The ^1H NMR analysis of the crude mixture indicated 45% of **7a**, 26% of **12b**, and 30% recovery of NCCH(Me)CO_2Et. By TLC (C_6H_6) was isolated 38% of **7a**: mp 82−83 °C (from petroleum ether/CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.29 (d, J = 9.0 Hz, 2 H), 7.68 (d, J = 9.0 Hz, 2 H), 4.32 (m, 2 H), 1.77 (s, 3 H), 1.57 (s, 3 H), 1.56 (s, 3 H), 1.38 (t, J = 7.1 Hz, 3 H); IR (KBr) 2240, 1737, 1680, 1524, 1351 cm^{-1}. Anal. Calcd for $C_{16}H_{18}N_2O_5$: C, 60.36; H, 5.71; N, 8.80. Found: C, 60.56; H, 5.61; N, 8.87.

By TLC was also isolated, at lower R_f than **7a**, **12b** in 21% yield (^1H NMR and IR spectra in agreement with the literature[7]).

The reaction was conducted in ordinary laboratory light (40 s). The ^1H NMR analysis of the crude mixture indicated 7% of **7a**, 70% of **12b**, and 69% recovery of NCCH(Me)CO_2Et. In the manner for the irradiated reaction was isolated **7a** in 4% yield (mp 79−81 °C) and **12b** in 65% yield.

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(19) Stevens, C. L.; Ettling, B. V. *J. Am. Chem. Soc.* **1955**, *77*, 5412−5414.
(20) *Beilsteins Handbuch der Organischen Chemie*: Vol. 1, Suppl. 1, 352e.
(21) Stevens, C. L. *J. Am. Chem. Soc.* **1948**, *70*, 165−167.

Table 2. Effect of Added $S_{RN}1$-Mechanism Inhibitors on Alkylation Reactions of Nitrile Potassium Salts with α-Haloisobutyrophenones in DMSO[a]

α-haloisobutyrophenone	nitrile anion	conditions	additive	*C*-alkylate yield,[b] %
1a	$(NCCHCO_2Et)^-$	25 °C, 7 h	none	22
		25 °C, 7 h	10 mol % $(t\text{-Bu})_2NO^\bullet$	19
1a	$[NCC(CH_3)CN]^-$	19 °C, 68 h	none	40
		19 C, 68 h	10 mol % $(t\text{-Bu})_2NO^\bullet$	33
1b	$[NCC(CH_3)CO_2Et]^-$	35 °C, 15 min	none	48
		35 °C, 15 min	10 mol % $(t\text{-Bu})_2NO^\bullet$	52
1b	$(Ph_2CCN)^-$	25 °C, 15 min	none	53
		25 °C, 15 min	5 mol % $m\text{-}C_6H_4(NO_2)_2$	48
		20 °C, 1 h[c]	none	83
		20 °C, 1 h[c]	20 mol % $(t\text{-Bu})_2NO^\bullet$	71
2a	$[NCC(CH_3)CO_2Et]^-$	20 °C, 40 s	none	7
		hν,[d] 20–30 °C, 40 s	none	43
		hν,[d] 20–30 °C, 40 s	5 mol % $m\text{-}C_6H_4(NO_2)_2$	49
		hν,[d] 20–30 °C, 40 s	10 mol % $(t\text{-Bu})_2NO^\bullet$	0
2a	$[NCC(CH_3)CN]^-$	18 °C, 30 min	none	76
		18 °C, 30 min	10 mol % $(t\text{-Bu})_2NO^\bullet$	0
2b	$[NCC(CH_3)CO_2Et]^-$	20 °C, 25 s	none	77
		20 °C, 25 s	10 mol % $(t\text{-Bu})_2NO^\bullet$	47
		20 °C, 25 s	30 mol % $(t\text{-Bu})_2NO^\bullet$	15

[a] Reactions conducted with a 0.3 M initial concentration both in nitrile salt and α-haloisobutyrophenone, under N_2, and in ordinary laboratory light, except as indicated. [b] Crude yields by ^1H NMR with added internal standard. [c] In HMPA. [d] *hν*: irradiation with a 300-W sunlamp at ca. 15 cm.

From the reaction in solvent HMPA with sunlamp irradiation (5 min) was isolated, in the same manner, 66% of **7a** (mp 82–83 °C).

From reaction of the nitrile salt with α-bromo nitro ketone **2b** in DMSO (30 min) 72% of **7a** (mp 82–84 °C) was isolated by recrystallization of the crude reaction product in petroleum ether/CH_2Cl_2.

Methyl[α-(*p*-nitrobenzoyl)isopropyl]malononitrile (7b). From reaction of (NCCMeCN)K with **2a** in DMSO (6 h) was isolated, by recrystallization of the crude product in petroleum ether/CH_2Cl_2, 62% of **7b**: mp 123–126 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.30 (d, J = 8.9 Hz, 2 H), 7.80 (d, J = 8.9 Hz, 2 H), 1.91 (s, 3 H), 1.66 (s, 6 H); IR (KBr) 2240, 1680, 1521, 1349 cm^{-1}. Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.98; H, 4.84; N, 15.49. Found: C, 61.68; H, 5.01; N, 15.70.

Ethyl β-Acetyl-α-cyano-α-methylisovalerate (8a). Reaction of $(NCCMeCO_2Et)K$ with **3** in HMPA (5 h) followed by Kugelrohr distillation (ot 98 °C/0.07 Torr) gave 88% of **8a**: liquid; ^1H NMR ($CDCl_3$, 90 MHz) δ 4.25 (q, J = 7 Hz, 2 H), 2.22 (s, 3 H), 1.61 (s, 3 H), 1.42 (s, 6 H), 1.32 (t, J = 7 Hz, 3 H); IR (neat) 2230, 1737, 1704 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.53; H, 8.13; N, 6.63. Found: C, 62.77; H, 8.27; N, 6.91.

β-Acetyl-α,α-diphenylisovaleronitrile (8b). Reaction of $(Ph_2CCN)K$ with **3** in HMPA (0 °C, 1 h), followed by digestion of the crude product in petroleum ether and recrystallization of the resulting solid in petroleum ether/CH_2Cl_2, gave 50% of **8b**: mp 127–129 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.33 (m, 10 H), 2.23 (s, 3 H), 1.36 (s, 6 H); IR (KBr) 2225, 1703 cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.26; H, 6.92; N, 5.05. Found: C, 82.04; H, 6.89; N, 4.97.

Ethyl α,β-Dicyano-α-methylisovalerate (9a).[9a] Reaction of $(NCCMeCO_2Et)K$ with **4** in HMPA (23 h) followed by Kugelrohr distillation (ot 86–90 °C/0.06 Torr) gave 59% of **9a** [lit.[9a] bp 150 °C/20 Torr; ^1H NMR ($CDCl_3$, 90 MHz) δ 4.37 (q, J = 7 Hz, 2 H), 1.80 (s, 3 H), 1.61 (s, 3 H), 1.55 (s, 3 H), 1.37 (t, J = 7 Hz, 3 H); IR (neat) 2235, 1728 cm^{-1}].

α′,α′-Dimethyl-α-phenylsuccinonitrile (9b). (PhCHCN)K (4.3 mmol) reacted with **4** (3.0 mmol) in HMPA (11 mL; 0 °C, 2.5 h). The ^1H NMR analysis of the crude mixture indicated the presence of **9b** in 51% yield and of β-methyl-α-phenylcrotononitrile (Me_2C=CPhCN) in 16% yield. By column chromatography (hexane/C_6H_6 3:2) was isolated 42% of **9b**: mp 66.5–68 °C (from petroleum ether); ^1H NMR ($CDCl_3$, 90 MHz) δ 7.42 (s, 5 H), 3.89 (s, 1 H), 1.48 (s, 6 H); IR (KBr) 2230 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.22; H, 6.58; N, 15.21. Found: C, 78.43; H, 6.72; N, 15.20.

Me_2C=CPhCN[22] was eluted from the column earlier than **9b** unseparated from recovered $PhCH_2CN$, being identified by the presence of diagnostic absorptions in the ^1H NMR and IR spectra of the mixture, and GC-MS [^1H NMR ($CDCl_3$, 90 MHz) δ 7.33 (s, 5 H), 2.18 (s, 3 H), 1.84 (s, 3 H); IR (neat) 2205, 1622 cm^{-1}; MS (70 eV) m/z 157 (100%, $M^{\bullet+}$)].

α′,α′-Dimethyl-α,α-diphenylsuccinonitrile (9c).[9b] Reaction of $(Ph_2CCN)K$ with **4** in HMPA (0 °C, 1 h) followed by Kugelrohr distillation (ot 180–240 °C/0.4 Torr) gave 66% of **9c** [mp 132–133 °C (from petroleum ether/CH_2Cl_2, lit.[9b] mp 130–133 °C); ^1H NMR and IR spectra in agreement with the literature[9b]].

α-(Cyanodiphenylmethyl)cyclopentanecarbonitrile (10). $(Ph_2CCN)K$ reacted with **5** in HMPA (0 °C, 2 h). The ^1H NMR analysis of the crude mixture indicated the presence of **10** in 60% yield and the dehydrobromination product from **5**, α-cyclopentenecarbonitrile, in 40% yield. By Kugelrohr distillation (ot 95–185 °C/200 Torr) was collected a fraction mainly consisting of α-cyclopentenecarbonitrile [^1H NMR ($CDCl_3$, 300 MHz) δ 6.53 (m), in agreement with the literature[8]]. By column chromatography (hexane/C_6H_6 4:1) of the undistilled residue was isolated 26% of recovered Ph_2CHCN, eluted first, and 48% of **10**: mp 119–121 °C (from petroleum ether); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.59 (m, 4 H), 7.39 (m, 6 H), 2.27 (m, 4 H), 1.94 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.5, 128.7, 128.6, 128.3, 123.0, 120.4, 59.0, 50.3, 38.3, 24.9. IR (KBr) 2220 cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.87; H, 6.35; N, 9.78. Found: C, 84.03; H, 6.59; N, 9.95.

5,5-Dimethyl-3,4-diphenyl-2(5*H*)-furanone (11a).[12] (PhCHCN)K reacted with **1a** in HMPA with sunlamp irradiation (1.5 h). The resulting solution was diluted with aqueous 1 M HCl, extracted with Et_2O, and the Et_2O phases washed with H_2O; from the combined aqueous phases slowly crystallized **11a**, which was recrystallized from petroleum ether/CH_2Cl_2 being obtained in 81% yield [mp 159 °C (lit.[12] mp 155–156 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41 (m, 5 H), 7.24 (m, 5 H), 1.62 (s, 6 H); IR (KBr) 1743, 1660 (w) cm^{-1}; MS (70 eV) m/z 264 (65%, $M^{\bullet+}$), 221 (70%), 43 (100%)].

5,5-Dimethyl-4-(*p*-nitrophenyl)-3-phenyl-2(5*H*)-furanone (11b). From reaction between (PhCHCN)K and **2a** in DMSO with sunlamp irradiation (1 h) was isolated, in the manner for **11a**, 41% of **11b**: mp 164.5–165.5 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 8.30 (d, J = 9 Hz, 2 H), 7.45 (d, J = 9 Hz, 2 H), 7.30 (s, 5 H), 1.60 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.2, 163.0, 148.2, 139.3, 129.2, 129.1, 128.7, 128.5, 128.2, 124.2, 85.5, 25.4; IR (KBr) 1743, 1516, 1344 cm^{-1}; MS (70 eV)

(22) Jarrouse, J. *C. R. Seances Acad. Sci.* **1957**, *244*, 2515–2518.

m/z 309 (80%, $M^{\bullet+}$), 266 (100%), 43 (97%). Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.88; H, 4.90; N, 4.53. Found: C, 70.00; H, 4.81; N, 4.79.

Reaction of (Ph_2CCN)K with 1a: α-Hydroxyisobutyrophenone (12a).[23] The nitrile salt reacted with **1a** in DMSO with sunlamp irradiation (25 °C, 15 min). After the usual workup the ^1H NMR analysis of the crude mixture indicated 11% of the alkylation product **6e**, 53% of **12a**, and 53 and 14% recoveries of Ph_2CHCN and **1a**, respectively. By TLC (C_6H_6) was isolated, in order of decreasing R_f, 49% of Ph_2CHCN, 4% of **6e** (mp 117–118.5 °C), and 44% of **12a** [^1H NMR spectrum in agreement with the literature;[7] IR (neat) 3430, 1672 cm^{-1}].

The reaction under the same conditions, except that it was conducted in the dark (wrapping the flask with aluminum foil), similarly produced 9% of **6e**, 46% of **12a**, and 53% recovery of Ph_2CHCN (by ^1H NMR analysis).

Reactions of (Ph_2CCN)K with 2a and 2b. The nitrile salt reacted with α-chloro nitro ketone **2a** in DMSO with sunlamp irradiation (20 °C, 1.5 h). The resulting mixture was diluted with H_2O and extracted with Et_2O and $CHCl_3$ to dissolve a solid precipitate. The ^1H NMR analysis of the crude mixture indicated 89% of tetraphenylsuccinonitrile ($NCCPh_2CPh_2CN$), 50% of *p*-nitroisobutyrophenone (p-$O_2NC_6H_4COCHMe_2$), and 32% of the α-hydroxy nitro ketone **12b**. By digestion in boiling petroleum ether and recrystallization of the resulting solid in Me_2CO was isolated a 83% of $NCCPh_2CPh_2CN$ [mp 221–225 °C dec (lit.[24] mp 223–224 °C); ^1H NMR spectrum in agreement with the literature[9b]]. By TLC (C_6H_6) of the fraction soluble in petroleum ether was isolated 42% of p-$O_2NC_6H_4COCHMe_2$ [mp 48–50 °C (lit.[25] mp 51.8–52.3 °C); ^1H NMR spectrum in agreement with the literature[25]], and, at lower R_f, 28% of **12b** (^1H NMR spectrum in agreement with the literature[7]).

The precedent reaction under the same conditions, except that it was conducted in the dark (wrapping the flask with aluminum foil), similarly produced 86% of $NCCPh_2CPh_2CN$, 50% of p-$O_2NC_6H_4COCHMe_2$, and 23% of **12b** (by ^1H NMR analysis).

From reaction of the nitrile salt with α-bromo nitro ketone **2b** in DMSO with sunlamp irradiation (30 min) was isolated, working in the manner for the reaction with **2a**, 75% of $NCCPh_2CPh_2CN$, 23% of p-$O_2NC_6H_4COCHMe_2$, and 8% of **12b**.

Reaction of (p-$O_2NC_6H_4COCMe_2$)K with 2a. The potassium salt (generated from 0.3 mmol of both p-$O_2NC_6H_4COCHMe_2$ and *t*-BuOK) reacted with **2a** (0.3 mmol) in freshly distilled, anhydrous DMSO (1 mL) with sunlamp irradiation (1.5 h). After the usual workup the ^1H NMR analysis indicated 25% of the α-hydroxy nitro ketone **12b** and 9% of recovered p-$O_2NC_6H_4COCHMe_2$ [%'s based on (p-$O_2NC_6H_4COCMe_2$)K + **2a**].

Dimethyl (α-Benzoylisopropyl)malonate (14). Reaction of (MeO_2CCHCO_2Me)K with **1b** in HMPA (5 h) followed by TLC (C_6H_6) gave 28% of **14**: oil; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.45 (m, 5 H), 4.30 (s, 1 H), 3.73 (s, 6 H), 1.46 (s, 6 H); IR (neat) 1732, 1682 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.53. Found: C, 64.58; H, 6.59.

Reaction of (Ph_2CCO_2Me)K with 1b. The potassium salt reacted with **1b** in HMPA (1.5 h). The ^1H NMR analysis of the crude mixture indicated the presence of methacrylophenone [$PhCOC(Me)=CH_2$] in 46% yield. By TLC (C_6H_6) $PhCOC(Me)=CH_2$ could not be obtained pure [the ^1H NMR spectrum of the impure product showed expected absortions for the olefin: ($CDCl_3$, 90 MHz) δ 5.91 (m, 1 H), 5.63 (m, 1 H), 2.07 (m, 3 H), in agreement with the literature[26]]. The *C*-alkylation product was not found.

Ethyl α-Cyano-β-(*p*-nitrobenzoyl)isobutyrate (15). Reaction of ($NCCMeCO_2Et$)K with p-$O_2NC_6H_4COCH_2Cl$ in DMSO (45 min) followed by TLC (C_6H_6) gave 41% of **15**: mp 87–89 °C (from EtOH); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.32 (d, J = 8.6 Hz, 2 H), 8.09 (d, J = 8.6 Hz, 2 H), 4.30 (m, 2 H), 3.76 (d, J = 18.2 Hz, 1 H), 3.55 (d, J = 18.2 Hz, 1 H), 1.74 (s, 3 H), 1.35 (t, J = 7.1 Hz, 3 H); IR (KBr) 2240, 1740, 1696, 1529, 1346 cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O_5$: C, 57.92; H, 4.87; N, 9.65. Found: C, 57.73; H, 4.95; N, 9.51.

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