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REACTION OF CONJUGATED NITRO OLEFINS WITH AROMATIC COMPOUNDS: A NEW ACYLMETHYLATION OF AROMATIC COMPOUNDS

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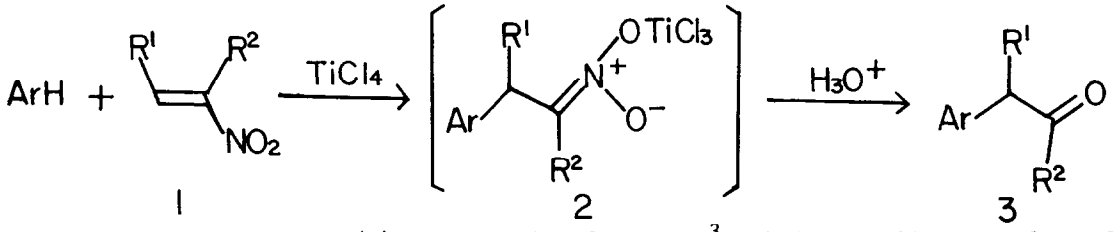
Summary: Reaction of conjugated nitro olefins with aromatic compounds, followed by hydrolytic treatment, gives acylmethylated aromatic compounds in good yield.

Direct acylmethylation of aromatic compounds by the electrophilic aromatic substitution reaction is usually very difficult.[1] This is presumably because the intermediary electrophilic complex of the Friedel-Crafts reaction inactivated by the neighboring electronegative acyl group. Recently, H. Ishibashi et al.,[2] reported the introduction of methylthiogroup to the acylmethyl halide greatly enhances the reactivity of the electrophilic complex. This method provides also a useful synthetic way because of the easily removable character of methylthio group. Here we wish to describe other convenient route to acylmethylation of aromatic compounds directly from conjugated nitro olefins in the presence of titanium tetrachloride.

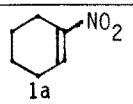
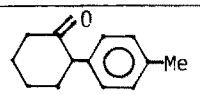
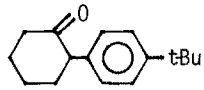
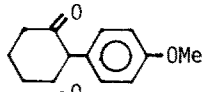
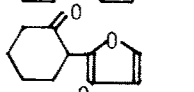
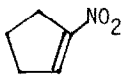
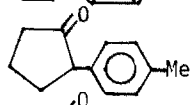
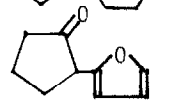
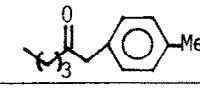


1 2 3

Conjugated nitro olefins (1) are good Michael acceptor[3] and they provide an umpolung of reactivity of carbonyl derivatives.[4] Therefore, we considered that the use of aromatic compounds as nucleophiles toward nitro olefins (1) in the presence of $TiCl_4$ would ideally be suited for the purpose since the feasible Michael-type adduct, nitronate intermediate such as (2), whould readily undergo the Nef reaction to give acylmethylated aromatic compounds (3) after hydrolytic treatment. The results are summarized in Table.

A typical experimental procedure is as follows: To a stirred solution of 1-nitro cyclohexene (2 mmol) in dry CH_2Cl_2(6 ml) was added toluene (10 mmol) at room temperature under nitrogen atmosphere. Titanium tetrachloride (2 mmol) was then added dropwise into the mixture with stirring at the same temperature. After being stirred for 30 min (The starting material completely disappears), water (3 ml)[5] was added and the resultant heterogeneous mixture was stirred at reflux for 2 hr. Normal work up gave the cyclohexanone-α-(4-methyl phenyl) (Entry 1), which was purified by short-path column chromatography on silica gel (8:2 hexane/ether).

Table. A new acylmethylation of aromatic compounds using conjugated nitro olefins[a]

Entry	Nitro Olefin	ArH	Product	Yield(%)[b]
1	 1a	Toluene		94
2	1a	t-Butyl benzene		86
3	1a	Anisole		90
4[c]	1a	Furan		72
5	 1b	Toluene		90
6[c]	1b	Furan		76
7		Toluene		62

[a]Reactions were performed as described in the text unless otherwise noted. [b]Isolated yield. [c]Reaction temperature was 0°C.

As shown in the Table, acylmethylated aromatic compounds are obtained in high yields and regioselectively (p-only by GLC and IR). Conjugated nitro olefins are readily available from the condensation of aldehydes with nitro alkanes, and alkenes.[6] Thus, this method should be an attractive route to acylmethylation of aromatic compounds.[7]

References and Notes

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4. D. Seebach, E.W. Colvin, and T. Weller, Chimia, 1979, **33**, 1.
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7. Conjugate additions of aryl group to nitro olefins are partly described in a recent paper. see: Angelo pecunioso and Rita Menicagli, J. Org. Chem., 1988, **53**, 45.

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