CHAPTER III

ALKYLATION OF METHYL NITROACETATE UNDER PTC
SUMMARY

It has been found that C-alkylation of methyl nitroacetate (13) can be best achieved by using triethyl benzyl ammonium chloride (TEBA) as phase transfer catalyst, potassium bicarbonate as base and DMF as a solvent. In the reaction of methyl nitroacetate (13) with benzyl bromide (27), methyl-2-nitro-3-phenyl propanoate (31) was the major product. However, O-alkylated product (38) and C,O-dialkylated product (39) also were formed in minor quantities.

In order to study the effect of substitution in aromatic nucleus of benzyl bromide (27) on product pattern, p-chloro (28), p-methoxy (29) and p-nitro (30) benzyl halides were reacted with methyl nitroacetate. Compound (28) and (29) furnished the C-alkylated products in good yields, however compound (30) afforded dialkylated products (37) and (41). In order to establish the generality of the reaction, simple alkyl halides, such as n-butyl bromide was treated with methyl nitroacetate (13) to give methyl-2-nitrohexanoate (43). Substituted ethyl nitroacetate (44) on reaction with benzyl bromide (27) gave ethyl-2-nitro 2-methyl-3 phenyl propanoate (45) in good yield.
Alkyl nitroacetates are promising intermediates for a number of compounds such as amino acids, nitroparaffins, amines and their derivatives. The presence of active methylene group makes these compounds unique intermediates for the formation of carbon-carbon bonds. Consequently, their reactivity often parallels that of other compounds containing an active methylene group. The nitro group is readily convertible to amino group and ester group is convertible to alcohol or methyl group. The alkyl nitroacetates are thus valuable intermediates for the synthesis of esters of 2-nitroalkanoic acids, nitro alcohols, nitro amines, halonitro compounds, di- and trinitro compounds, oxazolidines, oxazoles, amino acids, amino alcohols etc. The factors influencing the alkylation of alkyl nitroacetates have not been investigated thoroughly.

In recent past, there have been some attempts towards the alkylation of alkyl nitroacetates by classical methods which led to C-alkylated product in low yields (9-25%).

Hass and Bender have shown that alkylation of nitroparaffin salts may occur as C-alkylation forming new carbon-carbon bond or O-alkylation, leading to an unstable nitronic ester which breaks down into oxime and a carbonyl compound. Substituted benzyl halides when reacted with nitroparaffins yielded mainly substituted benzaldehydes which were attributed to formation of O-alkylation product.

Boyd and Kelly have reported alkylation of salts of ethyl nitromalonate (1) and ethyl nitroacetate (9) with allyl bromide (3) and crotyl chloride (4) (chart I). Thus potassium salt of ethyl nitromalonate (2) was heated in ethanol with allyl bromide (3) and crotyl chloride (4) to get ethyl allyl-
CHART I

\[
\begin{align*}
\text{R} - \text{C}-\text{NO}_2 \\
\text{COOEt} \\
\end{align*}
\]

1. R = H
2. R = K

\[
\begin{align*}
\text{R} - \text{CH}-\text{COOEt} \\
\text{NO}_2 \\
\end{align*}
\]

3. R = H
4. R = Na

CHART II

\[
\begin{align*}
\text{R} - \text{X} / \text{NaOEt} \\
\text{DMA} \\
\text{R} - \text{CH}-\text{COOEt} \\
\text{R} - \text{CH} - \text{CH}-\text{COOCH}_3 \\
\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{n-C}_4\text{H}_9, \text{n-C}_5\text{H}_{11}, \text{n-C}_7\text{H}_{15}
\end{align*}
\]

13. R = H, Cl, NO₂

14. R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, n-C₇H₁₅

15. R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, n-C₇H₃₅

16. R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, n-C₇H₃₅

17. R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, n-C₇H₃₅

18. R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, n-C₇H₃₅
nitromalonate (5) and ethyl crotylnitromalonate (6). These (5) and (6) on
decarboethoxylation with sodium ethoxide gave ethyl allylnitroacetate (7)
and ethyl crotylnitroacetate (8). Similarly sodium salt of ethyl nitroace-
tate (10) was reacted with allyl bromide (3) and crotyl chloride (4) to get
ethyl allylnitroacetate (7) and ethyl crotylnitroacetate (8). These were
then converted into their sodium salts (11) and (12) respectively. The yields
of alkylation are very low (10-11%). Zen and Kaji\(^5,6\) have synthesized α-
nitrodicarboxylates by C-alkylation of methyl nitroacetate with halo ester
of carboxylic acid. They have synthesised (DL)-aspartic acid, glutamic acid,
alanine, valine, phenyl alanine, lysine etc. It has been found that C-alkyl-
ation reaction of nitroacetates with halides take place only in dipolar aprotic
solvents such as DMF or dimethylacetamide.

A number of intermediates (14) (chart II) for the synthesis of amino
acids were prepared via C-alkylation of methyl nitroacetate (13) with substi-
tuted alkyl halides, with yields ranging from 11 to 88\(^7\). This alkylation
failed in protic solvents. Later it was reported that, use of n-alkyl iodides,
in addition to C-alkylated products (15), gave O-alkylated products which were
isolated as isoxazoline N-oxides (16) in 32-43%.

The study of alkylation of methyl nitroacetate was extended to p-substi-
tuted benzyl halides to produce 3-phenyl-2-hydroxyiminopropanoates
(17) (10-17%) and 3-phenyl-2-nitropropanoates (18) (20-37%)\(^8\).

Bocharova et al have reported\(^9,10\) alkylation of ethyl nitroacetate with
alkyl halides in presence of triethylamine to give 9-17% C-alkylated product.

The poor C-nucleophility of nitronate anions (20) can be dramatically
improved by formation of α,γ doubly deprotonated species (21)\(^11\). Solutions
of (21) are obtained by addition of two equivalents of n-butyl lithium to a solution of primary nitroalkane (19) in dry THF at -78°C in the presence of at least two equivalents of hexamethyl phosphoramide (HMPA). The dilithio derivatives (21) are smoothly alkylated to nitro alkanes (22) by primary alkyl and benzyl bromides and iodides in yields of 50-75% (chart III).

Because of great synthetic interest, the alkylation of carbanion is among the most extensively studied phase transfer catalysis (PTC) reactions. It was shown that the PTC method has many advantages over more conventional procedure which require not only expensive bases such as sodium amide, potassium tertiary butoxide, n-butyl lithium, metal hydrides etc. but also anhydrous solvents such as absolute ether, benzene, dimethyl sulfoxide, dimethyl formamide etc. In many cases PTC is simpler than other procedures and because it is highly selective, it gives good yields of purer products. Triethyl benzyl ammonium chloride (TEBA) is the most commonly used catalyst for such transformations.

Alkylation reaction of nitroacetate appears to commence with ambident anion and consequently carbon/oxygen atom can be alkylated as shown in chart IV. The extent of C-versus O-alkylation in alkyl nitroacetates depend upon the position of equilibrium between the two anionic species (23) and (24) generated from methyl nitroacetate (13) and their relative nucleophilicity towards the substrate.

To explain the preferential C-alkylation under PTC conditions, it is reasonable to assume that the reactive methylene and the halide ion from PTC form a hydrogen bonded complex (25) in which polarization towards carbanion occurs without the generation of full negative charge. Implication of this type of intermediate has been reported in the literature. This phenomenon also curbs the equilibration with species (26) encouraging thereby preferential C-alkylated product (chart IV).
\[ R' - CH_2 - NO_2 \rightarrow CH_2 - COOCH_3 \]

\[ R' - CH_2 - NO_2 \rightarrow CH_2 - COOCH_3 \]

\[ R^1 = H, C_2H_5, n-C_5H_{11}, C_6H_5, C_6H_5S \]
\[ R^2 = C_2H_5, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, C_6H_5CH_2 \]
PRESENT INVESTIGATION

Alkylation of alkyl nitroacetates has been carried out using phase transfer catalyst. It was found that alkylation of methyl nitroacetate (13) by benzyl bromide (27) using TEBA as catalyst and sodium hydroxide as base in polar and non-polar aprotic solvents like THF, methylene chloride, benzene, DMF etc. resulted in a complex reaction mixture. When bases like potassium carbonate and sodium carbonate were used in solvents like THF and DMF, it was found that nitro ester reacts with carbonates. It can be recovered after acidification. Here the alkylated product obtained is mainly C,0-dibenzyl (39) with little C,C-dibenzyl (35). When base like calcium hydroxide in THF was used, most of the nitro ester remained unreacted and no desired C-alkylated product (31) was obtained. With the use of optically active bases like sodium-potassium tartrate and dipotasium tartrate, the reaction was very slow and the product (31) was obtained in low yield with no optical induction. When potassium bicarbonate was used as a base in THF without TEBA catalyst only O-alkylated product (38) was isolated. In this reaction when TEBA was used, it showed formation of C-alkylated product (31). But when instead of THF, DMF was used as solvent only C-alkylated product (31) was obtained in 72\% yield. Among the different phase transfer catalysts like tetra n-butyl ammonium chloride, tetra n-propyl ammonium chloride and TEBA; TEBA was found to be suitable for C-alkylation than others (Table).

Thus C-alkylation can be best achieved by using TEBA as PT catalyst, dimethyl formamide as solvent and potassium bicarbonate as base.

In order to study the effects of substitution in aromatic nucleus of (27) on product pattern, p-chlorobenzyl chloride (28), p-methoxybenzyl bromide (29) and p-nitrobenzyl bromide (30) were reacted with methyl nitroacetate (13) under
CHART V

27 R = H, X = Br
28 R = Cl, X = Cl
29 R = OCH$_3$, X = Br
30 R = NO$_2$, X = Br

31 R = H
32 R = Cl
33 R = OCH$_3$
34 R = NO$_2$

35 R = R' = H
36 R = Cl, R' = H
37 R = R' = NO$_2$

38

39 R = R' = H
40 R = Cl, R' = H

41

Contd...
CHART V Contd.

\[ \text{A} \rightarrow \text{B} \]

\[ \text{C} \rightarrow \text{39 or 40} \]

\[ \text{n-C}_4\text{H}_9\text{Br} + 13 \rightarrow \text{C}_3\text{H}_7-\text{CH}_2-\text{CH}-\text{COOCH}_3 \]

\[ \text{42} \rightarrow \text{43} \]

\[ \text{CH}_3-\text{CH}-\text{COOC}_2\text{H}_5 + 27 \rightarrow \text{44} \]

\[ \text{44} \rightarrow \text{45} \]
the best conditions mentioned above. $p$-Chloro (28) and $p$-methoxy (29) compounds furnished the anticipated methyl-2-nitro-3-phenyl propanoates (32) and (33) in good yields (70% and 75% respectively). However, $p$-nitro-benzyl bromide (30) gave only dialkylated products methyl-2-nitro-2-($p$-nitro)-benzyl 3-($p$-nitro) phenyl propanoate (37) and methyl-2-nitro-3,4-bis ($p$-nitro phenyl)butanoate (41). It appears that compound (34) which itself was not found in the reaction mixture is the precursor for both (37) and (41). This is logical since carbanions at $C_2$ and $C_3$ in compound (34) are more stabilized due to nitro group as compared to (31). Intermediacy of compounds (31) and (32) was confirmed by converting (31) to $C$,C-dialkylated compound (35) under drastic conditions. Similarly (32) when reacted with benzyl bromide (27) furnished (36) and C,0-dialkylated compound (40). Structures of (39) and (40) were evident from the absence of $NO_2$ peaks and presence of C=N peak in IR. This was ably supported by mass and PMR spectra. These compounds are formed by elimination of Ph-CHO from the C,0,0-trialkylated species (C) (chart V). In order to establish the generality of the reaction, simple alkyl halides such as n-butyl bromide (42) was treated with (13) to give methyl 2-nitrohexanoate (43) in 72% yield. Substituted ethyl nitroacetate (44) yielded ethyl 2-nitro-2-methyl-3-phenyl propanoate (45) also in good yields (78%).
EXPERIMENTAL

Methyl nitroacetate (13) was prepared according to the procedure mentioned in the literature. p-Methoxy benzyl bromide (29) and p-nitro benzyl bromide (30) were prepared by standard procedures from corresponding toluenes, using N-bromo succinimide and benzoyl peroxide in carbon tetra chloride. The compounds used had following physical constants.

\[ \text{Ph-CH}_2\text{Br \ b.p. 195°C (lit. b.p. 199°C/749 mm)} \]
\[ \text{p-CH}_3\text{O-C}_6\text{H}_4\text{-CH}_2\text{Br b.p. 120°C/5 mm (lit. b.p. 106°C/2.5 mm)} \]
\[ \text{p-NO}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{Br m.p. 97°C (lit. m.p. 100°C)} \]
\[ \text{p-Cl-C}_6\text{H}_4\text{-CH}_2\text{Cl m.p. 28°C (lit. m.p. 29°C, b.p. 114-117°C/30 mm)} \]

General procedure for C-alkylation of methyl nitroacetate (13)

Alkyl halide (10 mmol) was added to a stirred solution of methyl nitroacetate (10 mmol) in dimethyl formamide (10 ml) containing TEBA (0.04 mmol) and anhydrous potassium bicarbonate (5 mmol). The reaction mixture was then stirred at 60°C for 16 hr. DMF was removed under reduced pressure and the mixture was diluted with water. It was then extracted with ether. Ether layer was washed with water and dried over anhydrous sodium sulfate. Removal of solvent furnished an oil, which was purified by distillation or column chromatography.

Methyl-2-nitro-3-phenyl propanoate (31)

Benzyl bromide (27, 1.71 g, 10 mmol), methyl nitroacetate (13, 1.21 g, 10 mmol), potassium bicarbonate (0.5 g, 5 mmole) TEBA (0.011 g, 0.04 mmol) afforded 1.49 g of (31), yield 70%; b.p. 80-90°C/0.4 mm; IR (neat) 1750, 1560, 1360 cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\)) 3.5 (d, 2H, CH-3, J=8 Hz), 3.7 (s, 3H COCCH\(_3\)), 3.78 (s, 3H COCCH\(_3\)), 3.83 (s, 3H COCCH\(_3\)).
5.28 (t, 1H, CH-2 J=8 Hz), 7.12-7.25 (m, 5H, Ar); MS 209 (M^+), 91 (Ph-CH\_2, 100%).

The PMR of crude reaction mixture shows the presence of O-alkylated product (38) and C,O-dialkylated product (39).

**Methyl-2-nitro-3-p-chlorophenyl propanoate (32)**

p-Chlorobenzyl chloride (28, 1.61 g, 10 mmol), methyl nitroacetate (13, 1.21 g, 10 mmol) furnished 1.1 g of (32), 70% yield after purification by column chromatography over silica gel using benzene : ethyl acetate (90:10); Rf 0.52 (EtOAc:benzene, 5:95); IR (neat) 1760, 1570, 1370 cm\(^{-1}\); \(^1\)H-NMR (CDCl\_3) 3.4 (d, 2H, CH\_2\^3, J=8 Hz), 3.8 (s, 3H, COOCH\_3), 5.25 (t, 1H, CH-2, J=8 Hz), 7.11 7.52 (m, 4H, Ar); MS 243 (M^+), 196 (M-HNO\_2), 125 (Cl-C\_6H\_4-CH\_2, 100%).

**Methyl-2-nitro-3-p-methoxy phenyl propanoate (33)**

p-Methoxybenzyl bromide (29, 0.402 g, 2 mmol), methyl nitroacetate (13, 0.238 g, 2 mmol), TEBA (0.0056 g, 0.02 mmol), potassium bicarbonate (0.1 g, 1 mmol) in DMF (10 ml) was stirred at 50°C for 4 hr, gave 0.352 g of (33), yield 74%; b.p. 110°C/0.02 mm; IR (neat) 1750, 1560, 1360 cm\(^{-1}\); \(^1\)H-NMR (CDCl\_3) 3.33 (d, 2H, CH\_2-3, J=8 Hz), 3.76 (s, 3H), 3.8 (s, 3H), 5.25 (t, 1H, CH-2, J=8 Hz), 6.7 and 7.06 (AB pattern, 4H, J=10 Hz); MS 239 (M^+), 121 (MeO-C\_6H\_4-CH\_2), 107 (MeO-C\_6H\_4); Analysis Found C, 55.31; H, 5.60; N, 5.93. C\_1\_1\_4\_3\_2\_N\_0 require C, 55.2; H, 5.43; N, 5.85.

**Methyl-2-nitro-2-(p-nitrobenzyl)-3-(p-nitro phenyl) propanoate (37) and methyl-2-nitro-3,4-bis (p-nitrophenyl) butanoate (41)**

p-Nitrobenzyl bromide (30, 2.16 g, 10 mmol), methyl nitroacetate (13, 1.21 g, 10 mmol), potassium bicarbonate (0.5 g, 5 mmol), TEBA (0.011 g, 0.04 mmol) in DMF (15 ml) was stirred for 2 hr at 50°C. Crude reaction mixture showed three spots on TLC. It was passed over silica gel column. Elution with benzene:EtOAc (90:10) afforded methyl-2-nitro-3,4-bis (p-nitrophenyl)
butanoate (41), 0.5 g, as an oil, b.p. 120°C/0.03 mm; IR (neat) 1760, 1530, 1350 cm⁻¹; ¹H-NMR (CDCl₃) 3.66 (d, 2H, CH-4, J=10 Hz), 3.87 (s, 3H, COOCH₃) 5.37 (d, 1H, CH-2, J=10 Hz), 5.44 (m, 1H CH-3), 7.31 to 8.35 (m, 8H, Ar). The positions of CH-2 and CH-3 were confirmed by decoupling; Analysis Found C, 52.12; H, 4.13; N, 10.62. C₁₇H₁₅N₃O₈ require C, 52.44; H, 4.08; N, 10.8.

Further elution with benzene:EtOAc (85:15) gave compound (37), 0.25 g, m.p. 165°C; IR (nujol) 1735, 1520, 1360 cm⁻¹; ¹H-NMR (CDCl₃) 3.8 (s, 4H, CH₂-3 and CH₂-4), 4.05 (s, 3H, COOCH₃), 7.26 and 8.14 (AB pattern, 8H, J=8 Hz); Analysis Found C, 52.81; H, 4.33; N, 11.21. C₁₇H₁₅N₃O₈ require C, 52.44; H, 4.08; N, 10.8.

Further elution with benzene:EtOAc (80:20 to 70:30) a compound was isolated. It showed no aromatic protons. It may be polymer of nitro ester. It was not investigated further.

Methyl-2-nitro-2-benzyl-3-phenyl propanoate (35)

Benzyl bromide (27, 0.427 g, 2.5 mmol) was added to a stirred solution of methyl-2-nitro-3-phenyl propanoate (31, 0.523 g, 2.5 mmol) in DMF (10 ml) containing TEBA (0.011 g, 0.04 mmol) and potassium carbonate (0.346 g, 2.5 mmol). The reaction mixture was stirred at 60°C for 16 hr. Usual work up afforded 0.950 g crude product. It was passed over silica gel column. Elution with benzene:EtOAc (90:10) furnished methyl-2-nitro-2-benzyl-3-phenyl propanoate (35), as an oil; Rf 0.72 (benzene:pet.ether-75:25); IR (neat) 1760, 1550, 1370 cm⁻¹; ¹H-NMR (CDCl₃) 3.44 (s, 4H, CH₂-3 and CH₂-4), 3.62 (s, 3H, COOCH₃) 7.0 – 7.37 (m, 10H, Ar); MS 299 (M⁺), 91 (C₆H₅CH₂, 100%).
Methyl-2-nitro-2-benzyl-3-(p-chlorophenyl) propanoate (36) and compound (40)

Reaction of benzyl bromide (27, 0.171 g, 1 mmol) and methyl-2-nitro-3(p-chlorophenyl)-propanoate (32, 0.243 g, 1 mmol) on similar treatment as described above, afforded a mixture of two compounds (0.3 g) which were separated by column chromatography over silica gel. Elution with benzene: EtOAc (90:10) afforded methyl-2-nitro-2-benzyl-3(p-chlorophenyl)propanoate (36) as an oil; Rf 0.75 (EtOAc:benzene, 5:95); IR (neat) 1750, 1550, 1360 cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\)) 3.42 (\(\delta\), 2H, CH\(_2\)), 3.48 (\(\delta\), 2H, CH\(^-\)S), 3.68 (\(\delta\), 13H, COOCH\(_3\)), 7.022 to 7.8 (m, 9H, Ar); MS 333 (M\(^+\)), 125 (Cl-C\(_6\)H\(_4\)-CH\(_2\)), 91 (C\(_6\)H\(_5\)-CH\(_2\), 100%).

On further elution with benzene: EtOAc (85:15 to 80:20) compound (40) was obtained as an oil, Rf 0.53 (EtOAc:benzene, 5:95); IR (neat) 1730, 1600(C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\)) 3.81 (\(\delta\), 3H, COOCH\(_3\)), 3.88 (\(\delta\), 2H, CH\(_2\)-3), 5.31 (\(\delta\), 2H, OCH\(_2\)), 7.15 to 7.35 (m, 9H, Ar); MS 317 (M\(^+\)), 125 (Cl-C\(_6\)H\(_4\)-CH\(_2\)), 91 (C\(_6\)H\(_5\)-CH\(_2\), 100%).

0-Alkylated product (38)

Benzyl bromide (27, 1.71 g, 10 mmol) was added to a stirred solution of methyl nitroacetate (13, 1.2 g, 10 mmol) in THF (10 ml) containing potassium bicarbonate (0.5 g, 5 mmol). The reaction mixture was refluxed for 12 hrs. The solvent was removed. Reaction mixture on usual work up gave an oil. It was distilled under reduced pressure, at 80-90°C/0.01 mm, 1.4 g (yield 70%); \(^1\)H-NMR (CDCl\(_3\)) 3.8 (\(\delta\), 3H, COOCH\(_3\)), 4.00 (\(\delta\), 2H, CH\(_2\)-2), 4.5 (\(\delta\), 2H, OCH\(_2\)), 7.33 (\(\delta\), 5H, Ar).

C,0-Dialkylated product (39)

Benzyl bromide (27, 1.71 g, 10 mmol) was added to a stirred solution of methyl nitroacetate (13, 1.2 g, 10 mmol) in THF (15 ml) containing TEBA
(0.0056 g, 0.02 mmol), potassium carbonate (2.8 g, 20 mmol). The reaction mixture was refluxed for 2 hrs. On usual work up it afforded an oil, which on column chromatography over silica gel gave C,0-dibenzyl compound (39) as an oil, 0.9 g (62%), b.p. 80°C/0.36 mm; Rf 0.35 (benzene); IR (neat) 1730, 1600 (C=N) cm⁻¹; ¹H-NMR (CDCl₃) 3.81 (s, 3H, COOCH₃), 3.93 (s, 2H, CH₂-3), 5.25 (s, 2H, OCH₃), 7.12 (s, 5H, Ar), 7.31 (s, 5H, Ar); MS 283 (M⁺), 224 (M-COOC₂H₅), 91 (C₆H₅CH₂, 100%).

Methyl-2-nitro-hexanoate (43)

Reaction was done according to general procedure for C-alkylation. Reaction was completed within 3 hr. On usual work up it gave an oil, which was chromatographed on silica gel to give the product (43) (yield 71.4%); IR (neat) 1770, 1570, 1380 cm⁻¹; ¹H-NMR (CDCl₃) 0.8 to 1.6 (m, 7H, aliphatic), 2.2 (m, 2H, CH₂-3), 3.8 (s, 3H, COOCH₂), 5.1 (m, 1H, CH-2): MS 175 (M⁺).

Ethyl-2-nitro propanoate (44)

It was prepared according to literature procedure, b.p. 95°C/3 mm (lit. b.p. 55°C/1 mm); IR (neat) 1760, 1560, 1350 cm⁻¹; ¹H-NMR (CDCl₃) 1.31 (t, 3H, -CH₂-CH₃, J=7.5 Hz), 1.81 (d, 3H, J=8 Hz), 4.25 (q, 2H, -CH₂CH₃, J=7.5 Hz), 5.13 (q, 1H, CH-2, J=8 Hz); MS 147 (M⁺), 101 (M-NO₂), 74 (M-COOEt).

Ethyl-2-nitro-2-methyl-3-phenyl propanoate (45)

Benzyl bromide (27, 0.281 g, 1.64 mmol) was added to a stirred solution of ethyl 2-nitro propanoate (44, 0.230 g, 1.64 mmol) in DMF (10 ml) containing TEBA (0.011 g, 0.04 mmol) and potassium carbonate (0.230 g, 1.64 mmol). The reaction mixture was heated at 50°C for 1.5 hr. Usual work up yielded an oil (0.39 g) which was passed over silica gel column. Elution
with benzene:EtOAc (90:10) gave the product, ethyl-2-nitro-2-methyl-3-phenyl propanoate (45) as an oil (0.286 g, 77%), Rf 0.25 (benzene); IR (neat) 1750, 1550, 1360 cm⁻¹; ¹H-NMR (CDCl₃) 1.28 (t, 3H, CH₂-CH₃, J=6 Hz), 1.68 (s, 3H, CH₃-2), 3.55 (d, 2H, CH₂-3, J=7 Hz), 4.28 (q, 2H, -CH₂-CH₃, J=6 Hz), 7.07 – 7.4 (m, 5H, Ar); MS 237 (M⁺), 91 (C₆H₅CH₂, 100%).

Table:
The percentage of different compounds (31), (38) and (39) by ¹H-NMR study-

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C-alkylated</th>
<th>O-alkylated</th>
<th>C,O-dialkylated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>integration</td>
<td>%</td>
<td>integration</td>
</tr>
<tr>
<td>TEBA</td>
<td>3.46</td>
<td>8</td>
<td>3.97</td>
</tr>
<tr>
<td>Tetra-n-butyl ammonium chloride</td>
<td>3.46</td>
<td>10</td>
<td>4.02</td>
</tr>
<tr>
<td>Tetra-n-propyl ammonium chloride</td>
<td>3.36</td>
<td>6</td>
<td>3.89</td>
</tr>
</tbody>
</table>

Signals corresponding to protons shown above are compared.
REFERENCES