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STUDIES ON ACID-CATALYSED σ-BOND CLEAVAGE OF AROMATIC CONJUGATED CYCLOPROPYL KETONES: A NEW SYNTHETIC ROUTE TO SOME HYDROAROMATIC SPIRO COMPOUNDS[1]

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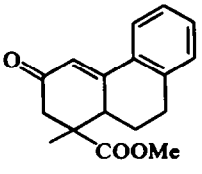
Abstract—Acid-catalysed cleavage of the aromatic conjugated cyclopropane σ-bond of the 3,4-benztricyclo[5.3.0^{1,7}.0^{2,7}]decan-10-one system has been studied and regioselective ring cleavage *via* the corresponding benzyl carbonium ion demonstrated giving rise to the respective spiro compounds.

Intramolecular keto-carbenoid insertion[2] reactions have found considerable applications in synthetic organic chemistry.[3] In connection with one of our projected syntheses of diterpene alkaloids, it was envisaged that an application of this method, followed by regioselective cleavage of the cyclopropane ring in the resulting product, such as 2, would provide a convenient route for the synthesis of a key intermediate (1) in this series.

Acid catalysed isomerisation of cyclopropane derivatives has been extensively studied[4] and it has been demonstrated[4a] on a few open chain aromatic substituted cyclopropyl ketones that the acid-catalysed cleavage proceeds through an intermediate benzyl carbonium ion (path a, Scheme 1). However, in the case of ring systems, such as 2, it



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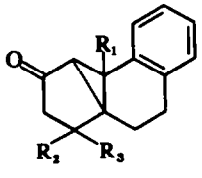

2: $R_1 = H$; $R_2, R_3 =$ 

3: $R_1 = R_2 = R_3 = H$

4: $R_1 = Me$; $R_2 = R_3 = H$

was not clear whether this, or an alternative mechanism involving a non-benzylic tertiary carbonium ion (path b) generated through participation of a different σ-bond of the cyclopropane ring would be predominant, as the benzyl carbonium ion, in such cases, would be secondary. If carbonium ion stability is deciding the reaction course, a tertiary benzyl carbonium ion, as can be encountered in 4, should favour the formation of a spiro derivative. To test these rationalities, with simultaneous exploration of ring opening to the synthetic objective, studies were undertaken on the acid-catalysed cleavage of cyclopropyl derivative 2, and two other model compounds 3 and 4. It has been established that in all these cases the cyclopropane ring cleavage takes place, exclusively *via* the intermediate benzyl carbonium ion.

Syntheses of starting materials for these studies were achieved by the general method[2] for intramolecular α-ketocarbenoid addition to an olefinic bond. Thus, the diazoketones derived from the unsaturated acids 5, 6 and 7 (experimental) were subjected to copper-bronze catalysed ring closure leading to formation of the desired cyclopropane 2, 3 and 4, isolated as crystalline solids in yields of 35%, 40% and 40% respectively. The tetracyclic ketone 4 was prepared earlier[7] through a photolytic reaction and its physical properties agreed closely with the recorded data.[7a] Compounds 2 and 3 were characterised by their spectral properties.

Treatment of 2, 3 and 4, in $CHCl_3$, with dry HCl resulted in the formation of chloro spiro ketones 8, m.p. 149–150° and 9, m.p. 114–115°, and the unsaturated ketone 11 as a liquid, in yields of 70%, 90% and 90% respectively. Structural proof for these products was derived through spectral data and on the basis of the following observations.

Catalytic reduction of 9 with 10% Pd/C in EtOH, as well as Li in liquid NH_3 reduction[8] of 3 afforded the cyclopentanone derivative 12 as a liquid, the structure of which was established through comparison with an authentic sample prepared independently (experimental). The unsaturated ketone 11 was earlier obtained by Chapmann *et al.*[7b] by photolysis of 4, and the reported spectral properties and melting point of a derivative agreed closely with our data. Further, catalytic reduction of 11 in

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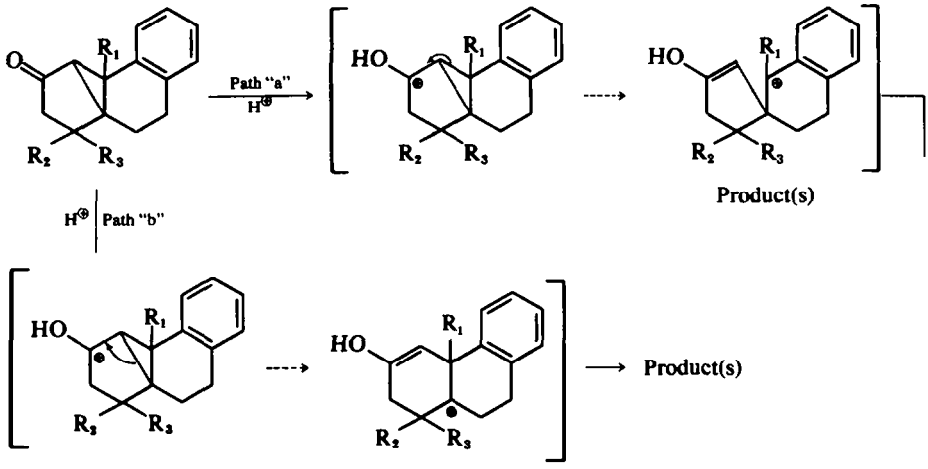
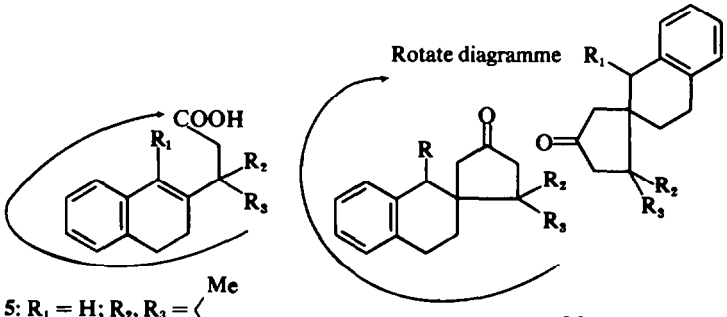
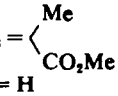


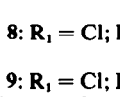
SCHEME 1. Possible Reaction Pathways.



5: $R_1 = H$; $R_2, R_3 =$ 

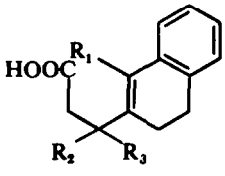
6: $R_1 = R_2 = R_3 = H$

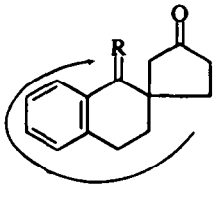
7: $R_1 = Me$; $R_2 = R_3 = H$

8: $R_1 = Cl$; $R_2, R_3 =$ 

9: $R_1 = Cl$; $R_2 = R_3 = H$

10: $R_1 = Me$; $R_2 = R_3 = H$

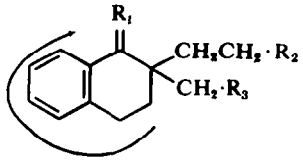




11: $R = CH_2$

12: $R = H_2$

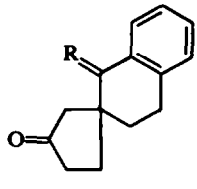
13: $R = O$

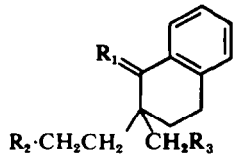


14: $R_1 = O$; $R_2 = CN$; $R_3 = CO_2Et$

15: $R_1 = O$; $R_2 = R_3 = CO_2H$

16: $R_1 = H_2$; $R_2 = R_3 = CO_2Et$





presence of 10% Pd/C furnished the saturated spiro ketone **10** as a liquid, which again was derived through the Li in liquid NH_3 reduction[8] of **4**. In the light of these observations and further supported by the spectral data, structure **8** was assigned to the product of cleavage of **2**.

The synthesis of an authentic sample of **12** was achieved, following the procedure described by Clarke *et al.*[9] for the preparation of the corresponding 6-methoxy compound. However, in a preliminary experiment where ethyl (1-oxo-1,2,3,4-tetrahydro-2-naphthyl)-acetate was condensed with ethyl acrylate in the presence of molar proportions of NaOEt in EtOH and the product subjected to acid hydrolysis, a neutral material was isolated as the only reaction product and characterised as **13** on the basis of spectral properties. This diketone, evidently obtained through a simultaneous Michael and Dieckman reaction, was catalytically reduced in the presence of perchloric acid to furnish ketone **12**.

These observations on regioselective cleavage of the aromatic conjugated cyclopropane σ-bond have been utilized in this laboratory[10] as one of the methods for the construction of some important tetracyclic intermediates, containing the bicyclo-[3.2.1]octane moiety, for the total synthesis of diterpenoids.

EXPERIMENTAL

All m.p.'s and b.p.'s are uncorrected. Light petroleum refers to the fraction b.p. 60–80°. All solvent extracts were finally dried over Na_2SO_4. All analytical samples were tested for purity by TLC.

UV spectra were determined on a Beckmann DU-spectrophotometer, in 95% EtOH. IR spectra were recorded as smears (liquids) or in $CHCl_3$ soln (solids), unless otherwise stated, on a Perkin-Elmer[21] double-beam recording spectrophotometer. PMR spectra were taken in 10–20% soln in $CDCl_3$ with TMS as the internal standard on a Varian A-60.

β-(3,4-Dihydro-2-naphthyl)-propionic acid (**6**) was prepared from β-(1-keto-1,2,3,4-tetrahydro-2-naphthyl)-propionic acid, m.p. 107–109° (lit.[11] m.p. 108–110°), according to the procedure described by Nakabayashi;[6] m.p. 95–96° (lit.[6] m.p. 96–97°).

β-(1-Methyl-3,4-dihydro-2-naphthyl)-propionic acid(**8**). To a stirred soln of MeMgI (0·05 mol) in 50 ml dry ether under N_2 at 5° was added a soln of β-(1-keto-1,2,3,4-tetrahydro-2-naphthyl)-propionic acid (4·4 g, 0·02 mol) in 50 ml dry ether over 1·5 hr. The soln was stirred at room temp for 1 hr, poured into 100 ml ice water and acidified with 5N HCl. The organic layer was separated and the aqueous mixture extracted with ether. The combined organic layers were washed with water, saturated $NaHCO_3$, and water and dried. Removal of solvent gave a gum which crystallised from a mixture of light petroleum and ether. The crude solid, 2·2 g (51%), m.p. 92–95°, was twice recrystallised from ether to afford **7** as colourless needles, m.p. 97–98°, λ_{max} 265 nm (log ε 4·15), ν_{max} 1710 cm^{-1} (—COOH); PMR: τ 7·91 (3H, s, $C_6H_5 \geqslant C—CH_3$). (Found: C, 77·55; H, 7·25. $C_{14}H_{16}O_2$ requires: C, 77·75; H, 7·46%.) The $NaHCO_3$ extracts on acidification with 2N HCl afforded the recovered keto acid, 1·5 g, m.p. 105–107°.

β-(3,4-Dihydro-2-naphthyl)-β-carbomethoxybutyric acid (**5**). This acid was prepared from the corresponding diester[5] by controlled hydrolysis. A soln of 15 g of the diester, 3·2 g KOH, 160 ml MeOH, and 8 ml water was heated at reflux for 4 hr under N_2. Partial solvent removal and work-up of the residue as usual gave a gum which crystallised from ether. The crude crystalline acid, 5·7 g (40%), m.p. 86–89°, was thrice recrystallised from light petroleum/ether to afford **5** as colourless needles, m.p. 91–92°, λ_{max} 265 nm (log ε 4·15), ν_{max} 1710 and 1725 cm^{-1}; PMR τ 3·6 (1 H, s, $C_6H_5—CH{=}CH_2$).

Syntheses of cyclopropyl ketones **2**, **3** *and* **4**. (a) *Diazoketone of acids* **5**, **6** *and* **7** were prepared according to the following general method.

To a suspension of the dry sodio-salt of the acid (0·01 mol) in 50 ml dry benzene was added dropwise 2·5 g (0·02 mol) oxalyl chloride at 5°. The mixture was allowed to stand for 3 hr, filtered, and the filtrate concentrated to afford crude acid chloride (100%) as a yellow oil.

The acid chloride (0·01 mol) in 40 ml dry ether was added dropwise to an ethereal soln of CH_2N_2 at 0°. The soln was allowed to stand for 4 hr. Removal of solvent at room temp yielded the corresponding crude diazoketone (100%) as a yellow semisolid, IR: characteristic peak at 2110–2160 cm^{-1}.

(b) *Intramolecular carbenoid addition.* The aforementioned crude diazoketones were cyclised according to the following general method of Stork and Ficini.[2a]

A soln of the corresponding crude diazoketone (0·01 mol) in 50 ml cyclohexane was added dropwise to a refluxing suspension of 2 g copper-bronze in 50 ml cyclohexane. After 18 hr reflux, the mixture was cooled and filtered and the catalyst washed with $CHCl_3$. The combined filtrate and washings were concentrated and the brown oily residue subjected to chromatography over neutral alumina.

Thus, *3,4-benz-8-methyl-8-carbomethoxy-tricyclo*[5.3.$0^{1,7}$.$0^{2,7}$]*decan-10-one* (**2**) was obtained as a crystalline solid (35% from **5**), m.p. 96–99°, from the eluants containing a mixture of light petroleum and benzene (3:1). Recrystallisation from a mixture of light petroleum and ether afforded an analytical sample of **2**, m.p. 101–102°, λ_{max} 234 nm (log ε 4·06); ν_{max} 1718 and 1680 cm^{-1}; PMR: τ 2·85 (4 H, aromatic), 6·24 (3 H, s, ester Me), 7·38 (2 H, benzylic), 7·55 (1 H, d, *J* 2·5 Hz, benzylic methine of cyclopropane ring), 7·67 (2 H, s, five-membered keto methylene), 7·72 (1 H, s, methine α to carbonyl), 8·1 (2 H, methylene β to aromatic), and 8·62 (3 H, s, quaternary Me). (Found: C, 75·67; H, 6·77. $C_{17}H_{18}O_3$ requires: C, 75·53; H, 6·71%.)

The tetracyclic ketone **3** was, similarly, isolated (40% from **6**) from eluants consisting of a mixture of light petroleum and benzene (1:1) as a crystalline solid which was recrystallised from light petroleum to afford a pure sample, m.p. 130–131°, λ_{max} 235 nm (log ε 4·07); ν_{max} 1718 cm^{-1}; PMR: τ 2·87 (4 H, m, aromatic), 7·36 (2 H, m, benzylic), 7·55 (1 H, d, *J* 2·2 Hz, benzylic methine of cyclopropane ring), 7·81 (4 H, s, five-membered ring methylenes), 7·88 (2 H, d, *J* 1·2 Hz, methylene β to aromatic), and 7·96 (1 H, d, *J* 3 Hz, methine α to carbonyl). (Found: C, 84·92; H, 7·29. $C_{14}H_{14}O$ requires: C, 84·81; H, 7·12%.)

Similarly the tetracyclic ketone **4** was isolated (40% from **7**) as crystalline solid from eluants consisting of a mixture of light petroleum and benzene (3:1) which was recrystallised from ether to afford an analytical sample

m.p. 88–90° (lit.[7a] m.p. 88·5–89·5°), λ_{max} 240 nm (log ϵ 4·01); ν_{max} 1712 cm^{-1}; PMR: τ 2·91 (4 H, m, aromatic), 7·38 (2 H, m, benzylic), 7·75 (4 H, m, five-membered ring methylenes), 7·94 (1 H, s, methine α to carbonyl), 7·99 (2 H, s, methylene β to aromatic), and 8·43 (3 H, s, quaternary Me). (Found: C, 84·80; H, 7·63. Calc. for $C_{15}H_{16}O$: C, 84·87; H, 7·60%.)

Cyclopropyl bond cleavage of tetracyclic ketones **2**, **3** *and* **4** *with dry hydrogen chloride.* A brisk stream of dry HCl gas was bubbled through a soln of the cyclopropyl ketone (0·01 mol) in 50 ml dry $CHCl_3$ at room temp for 1 hr. The solvent was removed and the product obtained in pure form as follows:

The crude chloro spiro ketone **8**, obtained as a solid from the aforementioned experiment was recrystallised from ether to afford a pure sample of **8** (65%), m.p. 149–150°, ν_{max} 1740 and 1725 cm^{-1}; PMR: τ 2·8 (4 H, s, aromatic), 4·93 (1 H, d, J 1·8 Hz, $C_6\underline{H}_5 \geq C\underline{H}Cl$), 6·27 (3 H, s, —COO$C\underline{H}_3$), and 8·45 (3 H, s, quaternary Me). (Found: C, 66·62; H, 6·30. $C_{17}H_{19}O_3Cl$ requires: C, 66·55; H, 6·19%.)

Similarly, the crystalline product from HCl treatment of **3** was recrystallised from ether to afford a pure sample of chloro ketone **9** (90%), m.p. 114–115°, $\lambda_{max}^{CHCl_3}$ 268 nm (log ϵ 2·89); ν_{max} 1740 cm^{-1}; PMR: characteristic doublet centered at τ 5·02 (1 H, d, J 1·2 Hz, $C_6H_5 \geq C\underline{H}Cl$). (Found: C, 71·40; H, 6·26. $C_{14}H_{15}OCl$ requires: C, 71·64; H, 6·39%.)

The unsaturated spiro ketone **11**[7b] was obtained as a liquid (90%) through aforementioned acid treatment of **4***, b.p. 140° (bath temp)/0·25 mm, λ_{max} 250 nm (log ϵ 4·1); ν_{max} 1740 cm^{-1}. The 2,4-dinitrophenylhydrazone (EtOAc) melted at 203–204°, (Found: C, 64·30; H, 4·92. $C_{21}H_{20}O_4N_4$ requires: C, 64·27; H, 5·14%). Treatment of **11** with benzaldehyde and base afforded two isomeric dibenzal derivatives, (a) m.p. 136–138° (lit.[7b] m.p. 136·5–138·5°); and (b) m.p. 172–174° (lit.[7b] m.p. 173–175°).

Catalytic hydrogenation of **9** *and* **11**. Hydrogenation of the chloro spiro ketone **9** (1 mmol) over Pd/C (10%; 100 mg) in 20 ml EtOH (completed in 30 min) and usual work-up of the mixture afforded spiro ketone **12** (93%) as a colourless liquid, b.p. 125–126° (bath temp)/0·2 mm, λ_{max} 250 nm (log ϵ 2·78), 266 nm (log ϵ 2·84), and 274 nm (log ϵ 2·87); ν_{max} 1740 cm^{-1}; *semicarbazone* m.p. 209–210°, m.m.p undepressed.

Spiro ketone **11** when similarly hydrogenated afforded saturated ketone **10** (95%) as colourless liquid, b.p. 142° (bath temp)/0·3 mm, λ_{max} 258 nm (log ϵ 2·93), 266 nm (log ϵ 2·95), 273 nm (log ϵ 2·94), and 277 nm (log ϵ 2·81); ν_{max} 1740 cm^{-1}; *2,4-dinitrophenylhydrazone*, m.p. 201–202°, (Found: C, 63·84; H, 5·72. $C_{21}H_{22}O_4N_4$ requires: C, 63·94; H, 5·62%.)

Reduction of **3** *and* **4** *with lithium in liquid ammonia.* The reaction was carried out in a three-necked flask, fitted with a dropping funnel and mechanical stirrer. Li wire (20 mg-atom) was added in pieces over 10 min to *ca.* 150 ml of well-stirred anhydrous liquid NH_3. To this was added a soln of cyclopropyl ketone (1 mmol) in 30 ml dry ether. The mixture was stirred for 1 hr then 12 g of solid NH_4Cl slowly added and the ammonia allowed to evaporate. The residue was treated with 100 ml of moist ether and the mixture carefully acidified with 6N HCl. The ether layer was separated and the aqueous mixture extracted with ether. The combined ethereal soln was washed with water and dried. The residue obtained on solvent removal was oxidised with Jones reagent,[12] and the product worked up as usual.

Reduction of **3** according as above afforded spiro ketone **12** (95%) as colourless liquid; semicarbazone m.p. 209–210°, m.p. with the derivative of **12** obtained from catalytic hydrogenation of **9** was undepressed. Similarly, reduction of **4** afforded saturated ketone **10** (85%) as a colourless liquid; 2,4-dinitrophenylhydrazone m.p. 201–202°, m.p. undepressed on admixture with the derivative of **10** obtained from catalytic hydrogenation of **9** as described earlier.

Synthesis of an authentic sample of **12**. The following synthesis is patterned after Clarke's[9] procedure for the preparation of the corresponding 6-methox compound.

1-Keto-2-(β-cyanoethyl)-2-carbethoxymethyl-1,2,3,4-tetrahydronaphthalene (**14**). To a soln of 11·6 g (0·05 mol) of ethyl (1-keto-1,2,3,4-tetrahydro-2-naphthyl)-acetate[13] in 75 ml dry benzene was added 3·1 g (0·06 mol) of NaOEt (from 0·1 g Na) in 0·5 ml of absolute EtOH under N_2 at 0°. The mixture was allowed to stand for 15 hr, refluxed for 2 hr, cooled, diluted with 50 ml water, acidified with 2N HCl. The mixture on usual work up afforded cyano ester **14**, 11·4 g (80%), as colourless oil, b.p. 180–182°/1 mm, ν_{max} 2270, 1730 and 1680 cm^{-1}, (Found: C, 71·82; H, 6·66. $C_{17}H_{19}O_3N$ requires: C, 71·56; H, 6·71%.)

1-Keto-2-(β-carboxyethyl)-2-carboxymethyl-1,2,3,4-tetrahydronaphthalene (**15**). A mixture of 11·4 g (0·04 mol) of cyano ester **14**, 50 ml glacial AcOH, 50 ml conc HCl, and 5 ml water were heated under reflux for 12 hr. The reagents were partially removed under reduced press, the residue diluted with 150 ml of water, and the mixture worked up in the usual manner to afford diacid **15**, 10 g (90%), m.p. 179–180° (EtOAc), (Found: C, 65·00; H, 5·84. $C_{15}H_{16}O_5$ requires: C, 65·21; H, 5·84%). The corresponding diethyl ester, prepared through treatment of **15** with EtOH in the presence of conc H_2SO_4, was obtained as a colourless liquid, b.p. 175–178°/0·5 mm, ν_{max} 1730 and 1680 cm^{-1}, (Found: C, 69·00; H, 7·45. $C_{19}H_{24}O_5$ requires: C, 68·65; H, 7·28%).

2-(β-Carbethoxyethyl)-2-carbethoxymethyl-1,2,3,4-tetrahydronaphthalene (**16**). A soln of the aforementioned keto diester (0·03 mol) in 50 ml EtOAc was subjected to hydrogenolysis over Pd/C (300 mg; 10%) in the presence of 0·2 ml $HClO_4$, and the mixture worked up in the usual manner to afford diester **16** (90%) as colourless viscous oil, b.p. 170–182°/0·5 mm, ν_{max} 1730 cm^{-1}, (Found: C, 71·75; H, 8·15. $C_{19}H_{26}O_4$ requires: C, 71·67; H, 8·23%).

Preparation of spiro ketone **12** *from diester* **16**. To a suspension of 0·42 g of Na dust in 35 ml of dry benzene was added dropwise under N_2 6·4 g (0·02 mol) of diester **16** at room temp. The mixture was heated under reflux for 5 hr, cooled, treated carefully with 5 ml EtOH, 50 ml water, and 5 ml conc HCl. The mixture was worked up in the usual manner and the crude liquid product treated with a mixture of 30 ml glacial AcOH, 30 ml conc HCl, and 5 ml water. The mixture was heated under reflux for 6 hr, the reagents partially removed, and the residue worked up in the usual manner to afford spiro ketone **12** (55% from **16**) as colourless liquid, b.p. 125–126°/0·2 mm, λ_{max} 250 nm (log ϵ 2·78), 266 nm (log ϵ 2·85), and 274 nm (log ϵ 2·85); ν_{max} 1740 cm^{-1}; (Found: C, 83·55; H, 8·30. $C_{14}H_{16}O$ requires: C, 83·96; H, 8·05%). *Semicarbazone* m.p. 209–210°, (Found: C, 69·78; H, 7·59. $C_{15}H_{19}N_3O$ requires: C, 70·00; H, 7·44%).

*In the communication[7b] **11** was reported to be obtained through acid treatment of **4**. However, the details of the reagents used were not mentioned.

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