Tetrahedron Vol 37, pp 615 to 620
© Pergamon Press Ltd. 1981. Printed in Great Britain

0040-4020/81/0201-0615/\$02.00/0

NITRO COMPOUNDS AS ALKYLATING REAGENTS IN FRIEDEL–CRAFTS CONDITIONS

REACTION OF 2-NITROPROPANE WITH BENZENE

V. Bonvino, G. Casini* and M. Ferappi
Istituto di Chimica Farmaceutica e Tossicologica, Università di Bari, Via Amendola 173, 70126 Bari, Italy

and

G. M. Cingolani and B. R. Pietroni
Istituto di Chimica Farmaceutica e di Chimica Organica, Università di Camerino, Italy

(*Received in UK* 27 *May* 1980)

Abstract—Friedel–Crafts reaction of benzylic or tertiary nitro compounds with benzene gave normal alkylation products. Similarly, 2-nitropropane (2-NP) gave cumene (**1**) which underwent further transformation affording a mixture whose behaviour with time was investigated: results were consistent with oxidative formation of the cumyl carbonium ion (**7′**).

In a previous communication,[1] we reported that benzylic (Scheme a) or tertiary (Scheme b) nitro compounds, i.e. compounds which were able to yield particularly stable carbonium ions after removing a nitrite anion, could react with excess benzene in the conditions of Friedel–Crafts reaction (1 mol $AlCl_3$) to give normal mono- or dialkylated products.

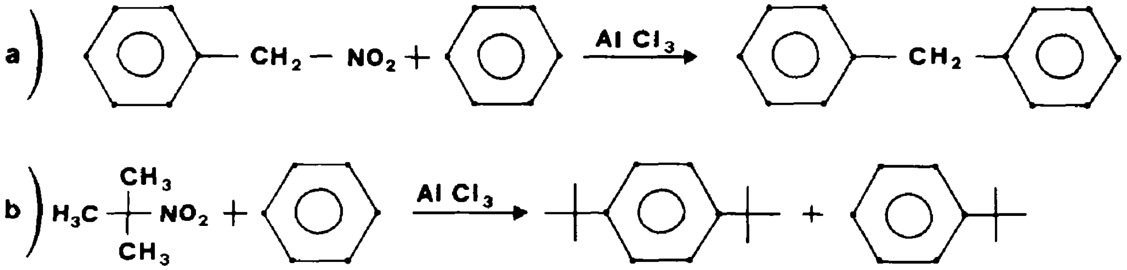
On the other hand, primary nitroalkanes did not react under similar conditions, whereas a secondary nitroalkane (2-nitro-propane = 2-NP) produced a mixture from which we could isolate a crystalline hydrocarbon identified as 3,3,3′,3′-tetramethylspiro-1,1′-biindane (**5**).[2-5]

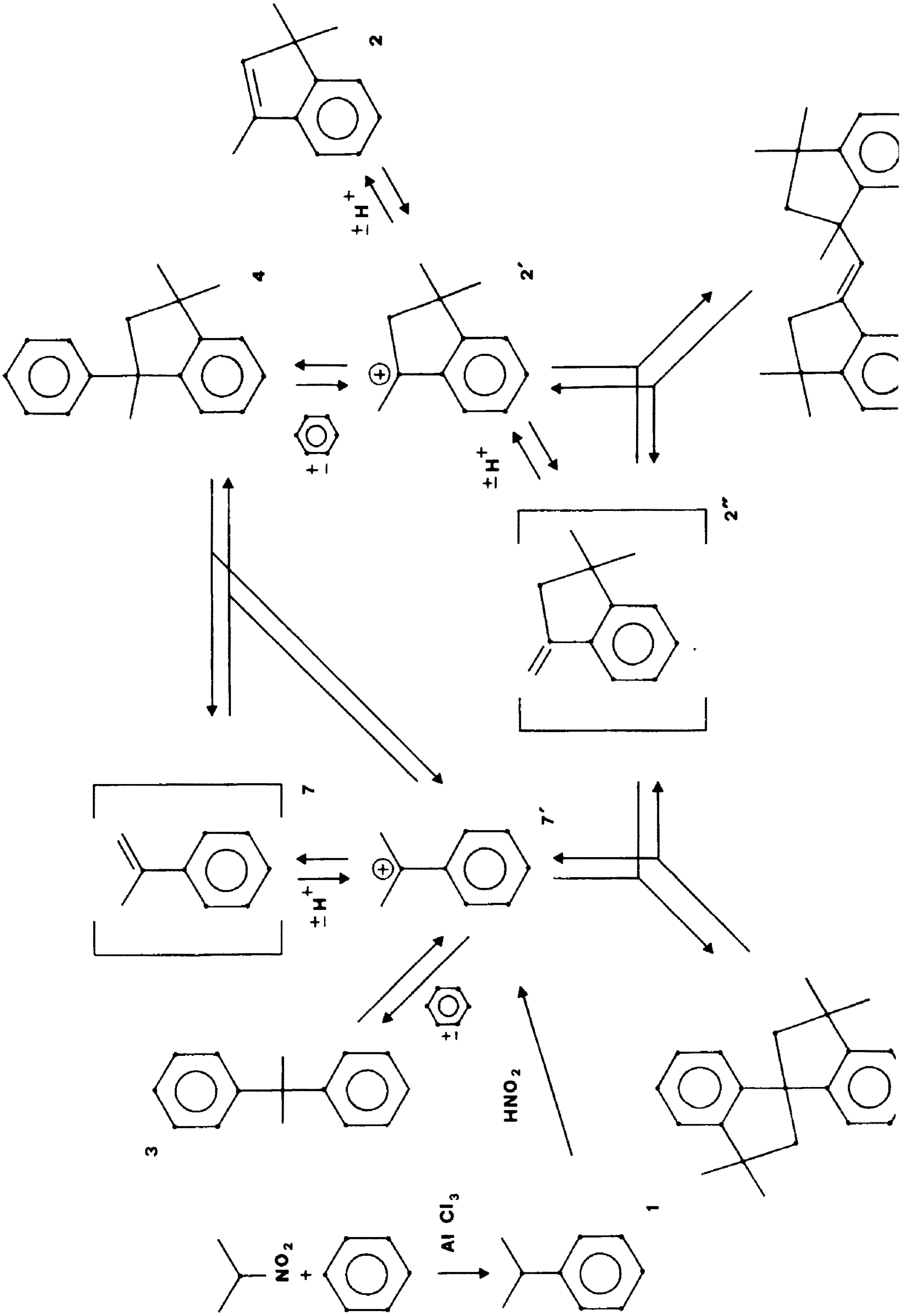
Since the formation of this hydrocarbon was not immediately interpretable, we decided to investigate the mechanism of this reaction. Various mixtures, obtained at different reaction times, were analysed by gas-chromatography. The main components, isolated through preparative gas-chromatography, were identified by NMR and mass spectrometry. The following compounds were found: cumene (**1**), 1,3,3-trimethyl-1-indene (**2**),[6] 2,2-diphenyl-propane (**3**),[7] 1-phenyl-1,3,3-trimethyl-indane (**4**),[8-10] 3,3,3′,3′-tetramethyl- 1,1′-spiro-biindane (**5**) (cited above) and 1′,3,3,3′,3′-pentamethyl-1-(1′-indanyl-methylene)-indane (**6**).[11]

Furthermore, it was found (Fig. 1) that cumene (**1**) and the two unsaturated compounds (**2** and **6**) were formed early and disappeared after long reaction times. The mixture became stabilized after 48 hr, yielding the three saturated compounds lacking benzylic hydrogens (**3**, **4**, **5**) in a yield ratio of 1:5:4 respectively.

Cumene is the only product whose formation can be explained by alkylation of benzene by the secondary carbonium ion deriving from 2-NP.

Figure 1 shows that cumene remained low in concentration only to disappear after a long period of time; apparently, it was rapidly consumed to form other components of the mixture. Most likely, it was transformed into a benzylic tertiary (cumyl) carbonium ion (**7′**), i.e. protonated α-methyl-styrene (**7**), since many of the compounds present in our mixture are known to be formed by allowing protic or aprotic acids to react with α-methyl-styrene (**7**)[8,10,12] or with its precursors like 2-phenyl-2-propanol,[3,7,13] 2-phenyl-2-chloro-propane[9] or even with its cyclic dimer (**4**).[14] By using other alkylating reagents (2-bromo-propane, 2-propanol) which would yield the same isopropyl carbonium ion as 2-NP in Friedel–Crafts conditions, it was possible to exclude hydride ion transfer[15,16] as a mechanism for the formation of **7′**. It has been reported,




NO₂
+
Al Cl₃
1
HNO₂
3
7
7′
±H⁺
±
4
2′
2″
2
±H⁺
±H⁺
±

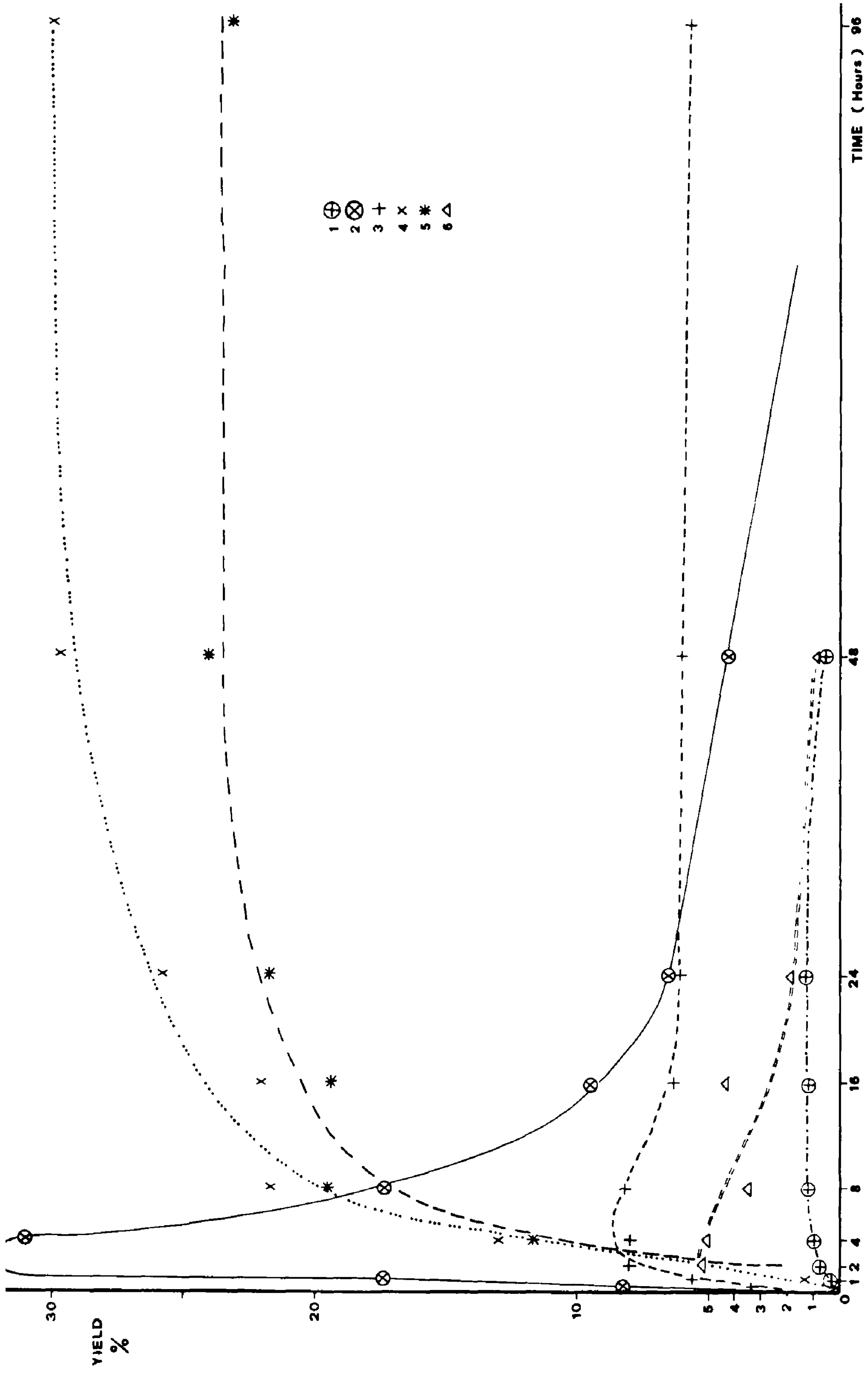
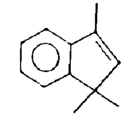
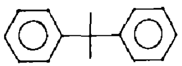
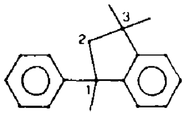
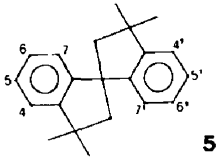
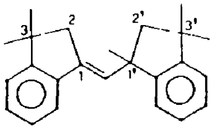


Fig. 1. Concentrations (expressed by "% Yields) of compounds 1, 2, 3, 4, 5, 6, in the reaction mixture from 2-NP + benzene, as a function of time.

Table 1. Physical and spectroscopic properties of components of reaction mixture from 2-NP + benzene

C O M P O U N D S	m.p. °C (solvent)	RETENTION TIME (min.) (*)	NMR(CCl_4/TMS); δ(ppm)	MASS SPECTRUM m/e (Abundance, % of base peak)
 **2**	LIQUID	9.40	1.18(s,6H,gem CH_3);1.95(d,3H,J=2Hz,CH_3) 5.81(q,1H,J 2Hz,CH)7.02(m,4H,arom.). (16)	158(53)M^+,144(13),143(100),141(18), 129(11),128(62),127(16),115(22).
 **3**	LIQUID	14.64	1.70(s,6H,gem.CH_3);7.13(s,10 H arom.). (16)	196(54)M^+,182(29),181(100),179(15), 178(13),166(54),165(45),115(11), 103(39),91(19),77(30). (16)
 **4**	52-53 (EtOH) (8,9,10)	16.62	1.08-1.38(2s,3H+3H,gem.CH_3)1.71(s,3H,1-CH_3); 2.18-2.41(AB syst.,2H,J=12.5Hz,CH_2)7.08(m.9H arom.). (16)	236(32)M^+,222(26),221(100),191(13), 178(12),165(11),143(83),129(11), 128(32),105(13),91(28).
 **5**	133-135 (EtOH) (2)	18.71	1.39-1.45(2s,6H+6H,gem.CH_3);2.25-2.32(AB syst., 4H,J=12.5Hz,CH_2);6.69(m,2H,7,7'-H);7.04(m,6H, rem.arom.). (12)	276(37)M^+,262(27),261(100),219(20), 217(12),216(12),215(21),205(12),203(11), 202(13),105(15),91(15). (12)
 **6**	40-43 (EtOH-petroleum ether)	23.42	1.15,1.17,1.18,1.21(4s,12H,gem.CH_3);1.31(s, 3H,1'-CH_3),1.03-1.29(AB syst.,2H,J=13,5Hz, 2'-CH_2)2.70(d,2H,J-1.5Hz,2-CH_2)5.68(t,1H, J=1.5Hz,CH)7.02(m,8H,arom.). (11)	316(1)M^+,160(13),159(100),141(7),129(12), 128(11),117(29),115(9),105(5),91(7). (11)

(*) COLUMN : 6.0 ft x 1/8 inc. STAINLESS STEEL,2% OV 101-0,2% CARBOWAX 20M on CHROM. W-HP 80-100; GAS FLOW : 25 ml/min.TEMP.PROGRAM.: 6',60°C ISOTHERM 10°C/min.up to 180°C, 20',180°C ISOTHERM.

however, that when a Me-homolog of cumene, i.e. *p*-cymene, reacts with nitrous anhydride in sulphuric acid,[17] it yields a dimer which is analogous to **4**. In this reaction *p*-cymene is apparently oxidized by nitrous anhydride into a benzylic tertiary carbonium ion and then forms the dimer. Therefore, it is quite possible that, in our case, the nitrite anion, or some other oxidizing species (nitrous acid, nitrogen oxides) deriving from 2-NP, transform cumene (**1**) into cumyl carbonium ion (**7′**), possibly through radical-cation intermediates.

Once cumyl carbonium ion (**7′**) has been formed, the formation of the other components can be easily explained, provided that there is complete reversibility of the electrophilic alkylation reactions under the conditions used (55) (Scheme C): **7′** may carry out an electrophilic attack on benzene to form **3**, or on α-methyl-styrene (**7**) produced by deprotonating **7′**—to yield the cyclic dimer (**4**); the latter may eliminate benzene to yield the indanylic carbonium ion (**2′**), which through deprotonation gives rise to two alkene isomers (**2** and **2″**), of which only the former is conceivably stable enough to be isolated and identified.

On the other hand **2″**, if present in adequate amounts, may undergo an electrophilic attack by **7′** to yield **5** and by **2′** to form the dimer of trimethyl-indene, i.e. **6**. The description of these mechanisms is similar to that formulated by Barclay[12] to explain the formation of **5**.

α-Methyl-styrene was not identified in our mixture; this was probably due to its easy polymerization,[8] also causing an incomplete overall yield of low molecular weight components (50% of the initial 2-NP).

The two unsaturated compounds (**2**, **6**) disappeared while the reaction proceeded, probably because they are thermodynamically less stable than the saturated compounds (**3**, **4**, **5**). To confirm the proposed reversible mechanisms, we carried out the reaction with a limited amount of benzene (stoichiometrically calculated to obtain **5**) in nitromethane as a solvent for 48 hr at 55 . The ratio of yields of the three final products (**3**, **4**, **5**), was shifted in favour of the last compound (1:2:10) under the new experimental conditions.

EXPERIMENTAL

General. Elemental analyses were carried out with a Hewlett Packard Model 185 C,H,N analyser, and were in agreement with molecular formulae of the hydrocarbons. The m.p., determined with a Tottoli apparatus, were not corrected. IR spectra were taken on a Perkin-Elmer 257 spectrophotometer as KBr pellets and were all in agreement with the hydrocarbon structures.

^{1}H-NMR spectra were recorded with a Varian HA 100 spectrometer, and the splitting patterns were indicated by symbols: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. The mass spectra were recorded with a Hewlett Packard 5992 G.C. mass spectrometer. Gas-chromatography analyses were carried out with a Hewlett Packard 5840A apparatus.

Conditions of Friedel Craft reactions. An ice-cooled suspension of freshly sublimed $AlCl_3$ (0.03 M) in anhyd benzene (10 ml) was added dropwise under magnetic stirring, with a soln of nitro compound (0.03 M) in 10 ml anhyd. benzene; nitrous vapour formation was observed; the mixture was allowed to warm to room temp. and eventually heated as described for the single nitro compounds. Working up was effected by pouring into ice and separating the organic phase which was washed with water and dried over Na_2SO_4. The soln was then tested by gas chromatography and treated for the isolation of the products as described for each compound.

(1) *Phenylnitromethane + benzene.* The mixture was stirred at room temp. for 24 hr. Tlc (Kieselgel 60 F_{254}, elution with benzene) showed absence of starting material and presence of benzaldehyde and of a spot with high R_f.

The product was isolated by column chromatography (silica gel 0.05 0.2, elution with benzene). The fraction corresponding to the high R_f spot crystallized completely: m.p. 26 27 . IR spectrum was identical to that of a pure sample of diphenyl-methane: the yield was 10%

(2) *2-Methyl-2-nitropropane + benzene.* The mixture was left at room temp. for 2 hr; no starting material could be detected by gas-chromatography, which showed a 40% yield of *t*-butylbenzene. On evaporating the solvent and the volatile fraction, a white solid residue remained, which could be crystallized from EtOH–water, m.p. 74–76 . This product was identified as *p*-di-*t*-butylbenzene by NMR and mass spectrometry, the yield 27%.

(3) *2-Nitropropane + benzene.* The mixture was kept for 2 hr at room temp. and then heated at 55 for various periods of time (0.5, 1, 2, 4, 8, 16, 24, 48 and 96 hr). During the first 2 4 hr, the mixture separated into two phases, the lower phase which was darker and contained a high concentration of unsaturated components, and the upper phase mainly presenting cumene and the products (**3**, **4**, **5**); whilst the unsaturated compounds disappeared, the mixture became homogeneous again

Figure 1 shows percent yields with respect to 2-NP determined by gas chromatography, referred to an internal standard (diphenyl) and to samples of pure compounds obtained by preparative gas-chromatography[a] from the mixture at the fourth hour: physical and spectroscopic data on these samples, as well as retention times in the analytical gas-chromatography conditions are reported in Table 1. Isolation of **5** could also be effected by evaporating the benzene soln of 24 hr reaction to dryness: the oily residue partly crystallized and the collected solid was crystallized from EtOH (Y ~ 20%).

The reaction was repeated using nitromethane as the solvent, whereby the amount of benzene corresponded to the molecular ratio 2:3 with 2-NP Reaction time was 48 hr; no phase separation was observed. Even though the overall yield was lower (~20%), the yield ratio was visibly shifted toward the spirobiindane product (Y_3:Y_4:Y_5 = 1:2:10).

The reaction was repeated also using 2-bromopropane or 2-propanol instead of 2-NP (time: 4 hr) giving a much simpler mixture in which **1** was present in fairly good concentration, but no trace of **2**, **3**, **4**, **5**, **6** could be detected.

REFERENCES

[1] G. Casini, M. Ferappi, G. M. Cingolani and B. R. Pietroni, *La Chimica e l' Industria* **56**, 463 (1974).
[2] A. Hoffman, *J. Am. Chem. Soc.* **51**, 2542 (1929).
[3] R. A. Barnes and B. D. Beitchman, *Ibid.* **76**, 5430 (1954).
[4] R. F. Curtis, *Chem. Ind.* 928 (1960).
[5] R. F. Curtis and K. O. Lewis, *J. Chem. Soc.* 418 (1962).
[6] J. Colonge and P. Garnier, *Bull. Soc. Chim. Fr* 436 (1948).
[7] K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.* **73**, 4766 (1951).
[8] H. Staudinger and F. Breusch, *Dtsch. Chem. Ber.* **62**, 442 (1929)

---

[a] Preparative gas-chromatography separation was effected with a Hewlett-Packard 5750 apparatus, equipped with a 8 ft × 3/10 in. column and a 1:20 splitter; gas flow was 400 ml min; stationary phase and temperature conditions were as for the analytical separation (see footnote in Table 1); one hundredth of the benzene soln was injected for each separation run.

[9] C. S. Schoepfle and J. D, Ryan, *J. Am. Chem. Soc.* **52**, 4021 (1930).

[10] E. Bergman, H. Taubadel and H. Weiss, *Dtsch. Chem. Ber.* **64**, 1493 (1931).

[11] H. A. Bruson and H. L. Plant, *J. Org. Chem.* **32**, 3356 (1967).

[12] L. R. C. Barclay and R. A. Chapman, *Can. J. Chem.* **42**, 25 (1964).

[13] L. H. Welsh and N. L. Drake, *J. Am. Chem. Soc.* **60**, 59 (1938).

[14] L. M. Adams, R. J. Lee and F. T. Wadsworth, *J. Org. Chem.* **24**, 1186 (1959).

[15] C. Serres and E. K. Fields, *Ibid.* **28**, 1624 (1963).

[16] R. Gelin and B. Chantegrel, *Bull. Soc. Chim. Fr.* 2527 (1971).

[17] N. Puranen, *Ann. Acad. Sci. Fenn.* 37A, No. 10, 1933 (*Chem. Abstr.* **27**, 5062 (1933)).