(6) P. Crabbé, E. Barreiro, J.-M. Dollat, and J.-L. Luche, *J. Chem. Soc., Chem. Commun.*, 183 (1976).

(7) The formation of alkane by dimerization of the alkyl groups attached to the copper was not reported in ref 4–6. Crabbé and co-workers[5,6] used dimethyl- and diethylcuprate, in which case ethane and butane could have easily escaped detection. Landor and co-workers[4] used di-*n*-buylcuprate in several reactions but did not report the formation of octane.

(8) W. H. Mandeville and G. M. Whitesides, *J. Org. Chem.*, **39**, 400 (1974).

(9) (a) D. E. Bergbreiter and G. M. Whitesides, *J. Org. Chem.*, **40**, 779 (1975); (b) D. E. Bergbreiter and J. M. Killough, *ibid.*, **41**, 2750 (1976).

(10) X. Creary, *J. Org. Chem.*, in press.

(11) This type of rearrangement has also been reported in ref 10.

(12) C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7783 (1973).

(13) R. G. Pearson and C. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976).

(14) Bisallenes were easily detected and isolated by GLPC techniques in the previous article.[3]

Synthesis of Highly Branched, β-Arylated Nitroparaffins[1]

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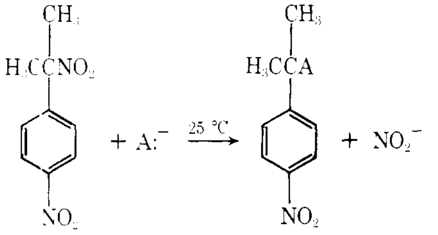
A synthetically useful one-step procedure for converting α-arylated tertiary nitro compounds into highly branched β-arylated nitroparaffins is described. These reactions appear to proceed via a chain mechanism in which radical anions and free radicals are intermediates.

Ten years ago it was discovered that the aliphatic nitro group of α,p-dinitrocumene (**1**) is readily displaced by a wide variety of nucleophiles as is shown in eq 1.[2] A large body of

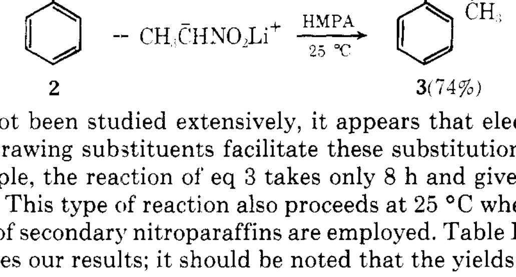


(1)

1

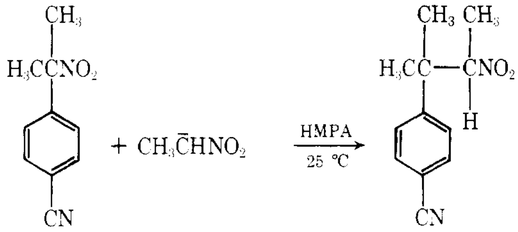
evidence now exists in support of the view that these are electron-transfer processes in which radical anions and free radicals are intermediates.[3] When the chemistry of α,p-dinitrocumene (**1**) was first described it was emphasized that the p-nitro group facilitates the displacements of eq 1; in no instance did α-nitrocumene (**2**) react with nucleophiles under conditions which resulted in complete reaction when α,p-dinitrocumene was employed.[2]

We have now found that the aliphatic nitro group of α-nitrocumene (**2**), and of substituted α-nitrocumenes and homologues thereof, can be displaced by nitroparaffin salts, albeit at a distinctly slower rate than when α,p-dinitrocumene is used. What is required is the use of hexamethylphosphoramide (HMPA) as the solvent, rather than the DMF or Me_2SO originally employed, and a relatively long reaction time (see Table I). Thus, in 45 h α-nitrocumene and the lithium salt of nitroethane react smoothly (eq 2). While the matter has not been studied extensively, it appears that electron-withdrawing substituents facilitate these substitutions; for example, the reaction of eq 3 takes only 8 h and gives 94% yield. This type of reaction also proceeds at 25 °C when the salts of secondary nitroparaffins are employed. Table I summarizes our results; it should be noted that the yields given there refer to pure, isolated products.



(2)

2 3(74%)



(3)

4 5(94%)

Simple, synthetically useful methods for preparing α-arylated tertiary nitro compounds are now available.[4,5] Consequently, the facile one-step conversion of α-arylated nitro compounds into highly branched β-arylated nitroparaffins makes the latter readily accessible. Manifestly, the synthesis of the highly ramified nitro compounds of Table I by classical means would be a matter of some difficulty. The relative insensitivity to steric hindrance of the processes of Table I is consonant with the view that they are radical anion reactions (vide infra) and serves to emphasize, once again, the utility of radical anion reactions for the preparation of highly branched structures.[3]

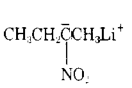
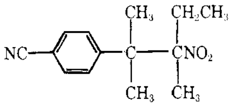
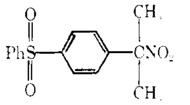
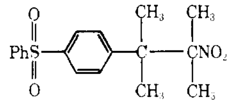
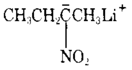
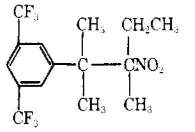
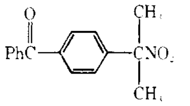
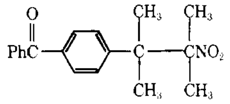
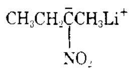
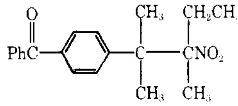
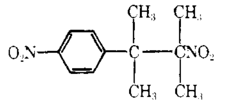
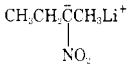
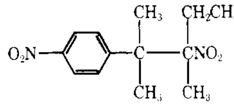
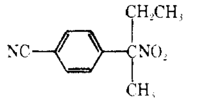
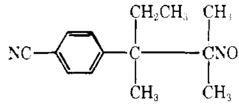
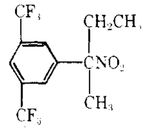
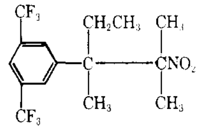
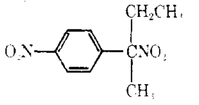
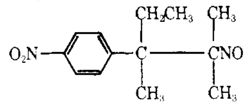
Several of the transformations listed in Table I have been studied in regard to the matter of mechanisms; in each case the characteristics of electron transfer substitution processes have been observed. Thus, the reaction of the lithium salt of nitroethane with α-nitrocumene (**2**) requires 45 h to proceed to completion and produces pure 2-phenyl-2-methyl-3-nitrobutane (**3**) in 74% yield (eq 2). But if di-*tert*-butyl nitroxide is present at the 9 mol % level the reaction is completely inhibited for 45 h. m-Dinitrobenzene (20 mol %) also retards this reaction; after 45 h it proceeds only 4% to completion. m-Dinitrobenzene is recognized as a diagnostic for radical anions,[1] di-*tert*-butyl nitroxide is a free-radical scavenger[1,6,7] and clearly the reaction of eq 2 is a chain process.

Two reactions employing p-cyano-α-nitrocumene (**4**) have also been investigated. At 25 °C the transformation of eq 3 requires 8 h and gives a 94% yield of the pure β-arylated nitroparaffin **5**. In contrast, if di-*tert*-butyl nitroxide is present at the 10 mol % level there is no reaction after 8 h and 91% of the p-cyano-α-nitrocumene is recovered. Furthermore, m-dinitrobenzene (20 mol %) completely inhibits this reaction for at least 8 h.

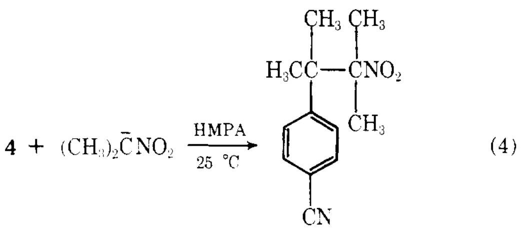
The second reaction of p-cyano-α-nitrocumene which was studied from the standpoint of mechanism is shown in eq 4; after 50 h a 68% yield of the pure β-arylated nitro compound

0022-3263/78/1943-1394$01.00/0

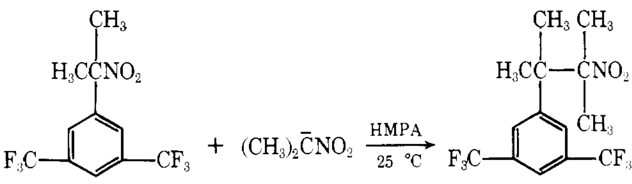
Table I. The Synthesis of β-Arylated Nitroparaffins at 25 °C[a]

α-Arylated nitro compd employed	Registry no.	Nitroparaffin salt employed	Registry no.	Reaction time, h	Product	Registry no.	% yield[b]
2	3457-58-7	$CH_3\bar{C}HNO_2Li^+$	28735-55-9	45	3	65253-35-2	74
4	58324-82-6	$CH_3\bar{C}HNO_2Li^+$		8	5	65253-36-3	94
4		$(CH_3)_2\bar{C}NO_2Li^+$	12281-72-0	50	6	65253-37-4	68
4		 $CH_3CH_2\underset{NO_2}{\bar{C}}CH_3Li^+$	35818-95-2	46		65253-38-5	68
	58324-84-8	$(CH_3)_2\bar{C}NO_2Li^+$		110		65253-39-6	71
7	58324-86-0	$(CH_3)_2\bar{C}NO_2Li^+$		16	8	65338-72-9	90
7		 $CH_3CH_2\underset{NO_2}{\bar{C}}CH_3Li^+$		45		65253-40-9	50
	58324-79-1	$(CH_3)_2\bar{C}NO_2Li^+$		72		65253-41-0	62
′′		 $CH_3CH_2\underset{NO_2}{\bar{C}}CH_3Li^+$		74		65253-42-1	61
1		$(CH_3)_2\bar{C}NO_2Li^+$		2[c]		14851-03-7	84
1		 $CH_3CH_2\underset{NO_2}{\bar{C}}CH_3Li^+$		6		65253-43-2	74
	65253-33-0	$(CH_3)_2\bar{C}NO_2Li^+$		92		65253-44-3	60
	65253-34-1	$(CH_3)_2\bar{C}NO_2Li^+$		45		65253-45-4	60
	58324-83-7	$(CH_3)_2\bar{C}NO_2Li^+$		3		65253-46-5	76

[a] All reactions were carried out in HMPA at 25 °C with exposure to light.[14] [b] Pure, isolated product. [c] M. M. Kestner, Ph.D. Thesis, Purdue University, May 1973.


6(68%)

(4)


7

8(90%) (5)

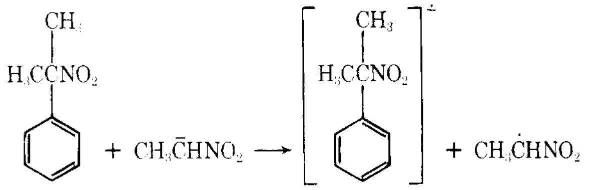
6 is isolated. As in the preceding cases, catalytic amounts of *m*-dinitrobenzene and di-*tert*-butyl nitroxide completely inhibit the reaction.

The process of eq 5 requires 16 h and gives a 90% yield of the β-arylated nitroparaffin 8. Here again complete inhibition is observed when *m*-dinitrobenzene (10 mol %) or di-*tert*-butyl nitroxide (8 mol %) are present; 98% of the initially employed α-nitrocumene 7 is recovered from the *m*-dinitrobenzene experiment and 85% from the one in which nitroxide is present.

The effect of light on these reactions is also noteworthy. All the transformations of Table I are conducted with exposure to the illumination of two ordinary 20-W fluorescent lamps. However, when α-nitrocumene (2) and the lithium salt of nitroethane are brought together under conditions which result in the reaction of eq 2, except that now the system is maintained in total darkness, no reaction occurs and 83% of the

α-nitrocumene is recovered. Nor is this a unique result; the reactions of eq 3 and 4 also do not occur in the absence of light. And while the reaction of eq 5 does proceed in the dark it is unambiguously speeded up by light (cf. Experimental Section). Although many electron-transfer substitution reactions take place in the dark they are often accelerated by light.[1] The dramatic light effects observed in the reactions of α-nitrocumene and p-cyano-α-nitrocumene, and the smaller one noted in the reaction of eq 5, are consonant with an electron-transfer mechanism.

The chain mechanism of eq 6–9 provides a simple basis for understanding the foregoing facts and is consistent with what is known about related processes.[1] Presumably, not only the reactions of α-nitrocumene, p-cyano-α-nitrocumene, and the fluorinated α-nitrocumene **7**, but also the reactions of the other α-arylated tertiary nitro compounds proceed via a radical anion–free radical chain sequence such as that shown in eq 6–9 for α-nitrocumene.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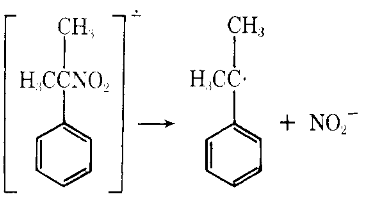
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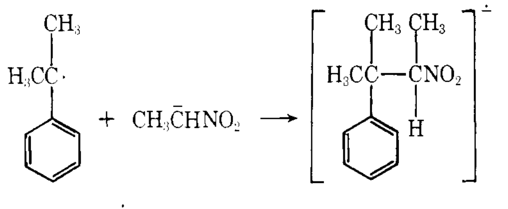
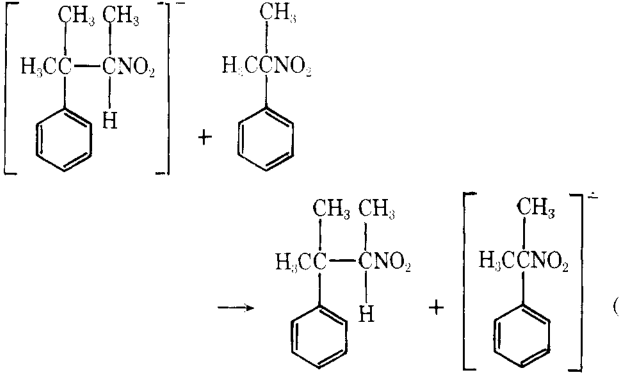
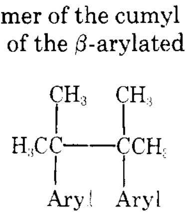
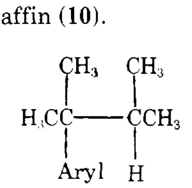

(8)


(9)

Finally, it should be pointed out that very small amounts of two byproducts are often produced in these reactions. One is the dimer of the cumyl radical (**9**), the other the reduction product of the β-arylated nitroparaffin (**10**).


9


10

In this connection the reaction of α-nitrocumene (**2**) with the lithium salt of 2-nitropropane is of interest. This reaction is very slow; after 6 days NMR analysis indicates that 22% of the α-nitrocumene is still unreacted, that the β-phenylated nitroethane (2,3-dimethyl-2-phenyl-3-nitrobutane) is formed in 30% yield, and that the bicumyl is produced in 48% yield. While these data are not definitive there can be little doubt that in this one case the desired reaction is not the major process.[21] That this is so appears to derive from a combination of steric and electrical effects. In the first place, as shown in eq 2, α-nitrocumene when treated with the lithium salt of nitroethane readily gives the β-arylated nitroparaffin and not the cumyl dimer. This suggests that the enhanced steric requirement in going from the anion of nitroethane to that of 2-nitropropane is a significant adverse influence. But, as can be seen from eq 5 and Table I, α-nitrocumenes bearing electron-withdrawing substituents react readily with the lithium salts of 2-nitropropane and 2-nitrobutane. Clearly, in these cases the steric factor is outweighed by a polar factor. One can only speculate as to how the polar factor operates; one possibility is that cumyl radicals bearing electron-withdrawing substituents possess heightened electrophilicity, so that the drive for reacting with a nitroparaffin anion to give a radical anion is greater than for the unsubstituted cumyl radical.

Experimental Section[8]

CAUTION: HMPA should be handled with great care since it has recently been found to cause cancer in laboratory animals [*Chem. Eng. News*, **54** (39), 17 (1975)].

α-Arylated Nitro Compounds. Most of the α-arylated nitro compounds employed in this study are known and their synthesis from substituted nitrobenzenes has been described.[4] The following preparations are new.

2-(p-Cyanophenyl)-2-nitrobutane. The lithium salt of 2-nitrobutane (10.9 g, 100 mmol),[9] p-cyanonitrobenzene (7.40 g, 50 mmol), 100 mL of HMPA, and a reaction time of 17 h were employed.[4] On workup 9.6 g of an orange oil was obtained. This was chromatographed through a short column of alumina using benzene as the eluent. The resulting 8.90 g of product, when Kugelrohr distilled at 1 mm and 120 °C, gave 8.81 g of a light yellow oil (87% yield): NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.96 (s, 3 H), 2.18–2.55 (m, 2 H), 7.35–7.85 (m, 4 H); IR (neat) 4.45 (CN), 6.49, 7.40 (NO_2) μm.

Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.69; H, 5.66; N, 13.54.

2-m,m'-Bis(trifluoromethyl)phenyl-2-nitrobutane. 3,5-Bis(trifluoromethyl)nitrobenzene (10.35 g, 39.77 mmol) and the lithium salt of 2-nitrobutane (4.70 g, 43.1 mmol) were allowed to react in 50 mL of HMPA under argon. Workup after 24 h and crystallization from hexane gave colorless crystals: mp 43–44 °C; NMR ($CDCl_3$) δ 0.97 (t, 3 H), 2.01 (s, 3 H), 2.48 (m, 2 H), 7.89 (br s, 3 H); IR ($CHCl_3$) 6.47, 6.85, 7.25 μm.

Anal. Calcd for $C_{12}H_{11}NO_2F_6$: C, 45.57; H, 3.83; N, 4.43; F, 36.06. Found: C, 45.35; H, 3.75; N, 4.23; F, 35.81.

α-Nitrocumene (**2**) was obtained from α-methylstyrene via the following intermediates.

***N*-α-Cumylformamide.** α-Methylstyrene (236 g) was subjected to the Ritter reaction;[10] 120 g (36% yield) of slightly impure N-α-cumylformamide was obtained. For analysis a small portion of the formamide was passed through silica gel using chloroform as the eluent; the first fraction was largely composed of an impurity. Continued elution with chloroform and then with ethyl acetate gave a yellow oil which after Kugelrohr distillation at 0.1 mm and 93 °C is colorless: $n^{23}{}_D$ 1.5371; NMR ($CDCl_3$) δ 1.53 (s, 3 H), 1.57 (s, 3 H), 7.0–8.2 (m, 7 H); IR (neat) 3.06 (NH), 3.65 (O=CH), 6.0 (C=O) μm.

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.44; H, 7.82; N, 8.40.

α-Aminocumene. This was obtained on alkaline hydrolysis of the formamide;[10] from 111.7 g of the slightly impure formamide, 61.9 g (67% yield) of pure α-aminocumene was isolated: bp 94 °C (26 mm); $n^{24}{}_D$ 1.5174 (lit.[11] $n^{25}{}_D$ 1.5175–1.5185); NMR ($CDCl_3$) δ 1.41 (s, 8 H), 7.1–7.2 (m, 5 H); IR (neat) 2.98, 3.07 (NH_2) μm.

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 80.03; H, 9.74; N, 10.55.

α-Nitrocumene (2). Permanganate oxidation[12] of 59.9 g of α-aminocumene gave 34.6 g (47% yield) of pure α-nitrocumene: bp 97 °C (5 mm); $n^{25}{}_D$ 1.5178 (lit.[5] $n^{20}{}_D$ 1.5204); NMR ($CDCl_3$) δ 1.95 (s, 6 H), 7.39 (s, 5 H); IR (neat) 6.55, 7.44 (NO_2) μm.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.60; H, 6.72; N, 8.50.

β-Arylated Nitroparaffins. General Procedure. The synthesis of compound 8 (the reaction of eq 5) is illustrative. The center neck of a 200-ml three-neck flask is fitted with an adapter constructed of a male and a female ground-glass joint separated by a stopcock. Each of the other two necks is fitted with an addition tube (A). These addition tubes are so constructed that their contents may be emptied into the flask without opening the system, merely by rotating around the joint (cf. Figure 1). One of the addition tubes is charged with 2.989 g (10 mmol) of 3,5-bis(trifluoromethyl)-α-nitrocumene (**7**)[4] and the other contains 4.75 g (50 mmol) of the lithium salt of 2-nitropropane;[13,9] a magnetic stirring bar and 100 mL of HMPA are placed in the flask.

The system is purged of air by evacuating and then bleeding in argon. This process is repeated three times and then the HMPA is frozen by liquid nitrogen. The system is evacuated to ~1 mm and the frozen HMPA is allowed to thaw. This freeze–pump–thaw procedure is repeated two more times and then argon at 1-atm pressure is bled in. [This rigorous degassing is probably not necessary in most cases. An alternative is to purge the system of air simply by evacuating and then bleeding in nitrogen; this procedure is repeated three times. A number of the reactions of Table I were run both "freeze–pump–thaw" and "under nitrogen" with identical results.]

The flask is placed under the light apparatus,[14] magnetic stirring is instituted, and the 2-nitropropane salt is added. After the salt has dissolved the 3,5-bis(trifluoromethyl)-α-nitrocumene (**7**) is added and the resulting solution is stirred for 16 h at room temperature. The solution is then poured into water and extracted with benzene. The benzene phase is washed with water and dried over anhydrous $MgSO_4$, and then the solvent is removed using a rotatory evaporator under reduced pressure. The resulting yellow oil (3.38 g) is dissolved in 15 mL of hexane and chromatographed on alumina. Elution with hexane quickly gives 0.08 g (2% yield) of a colorless liquid which has an NMR spectrum identical with that of authentic 2,3-dimethyl-2-[*m,m'*-bis(trifluoromethyl)phenyl]butane;[15] that is immediately followed by 0.06 g (1% yield) of the *m,m'*-bis(trifluoromethyl)cumyl dimer: mp 66.5–68 °C (lit.[16] mp 67–68 °C). Further elution with 90% hexane–10% benzene gives 3.06 g (90% yield) of the β-arylated nitroparaffin **8**: colorless crystals; mp 49–50 °C; NMR (CCl_4) δ 1.50 (s, 6 H), 1.57 (s, 6 H), 7.77 (br s, 3 H).

Anal. Calcd for $C_{14}H_{15}F_6NO_2$: C, 48.99; H, 4.40; F, 33.21; N, 4.08; mol wt, 343. Found: C, 49.02; H, 4.41; F, 33.04; N, 4.08; mol wt, 344.

The reaction between 3,5-bis(trifluoromethyl)-α-nitrocumene (**7**) and the lithium salt of 2-nitropropane was also studied as regards the matter of mechanism. A duplicate of the foregoing experiment was carried out except that now 0.168 g (1 mmol) of *m*-dinitrobenzene was present. From the crude red-brown product (3.247 g) a total of 2.975 g (98% recovery) of pure 3,5-bis(trifluoromethyl)-α-nitrocumene (**7**) was obtained by recrystallization from hexane and chromatography on alumina: mp 54–55 °C. The NMR spectrum of this recovered material was identical with that of the starting material and it was pure by VPC. Thus, complete inhibition had occurred.

Another duplicate of the first experiment was carried out except that here di-*tert*-butyl nitroxide was present (0.110 g, 0.8 mmol). On workup and purification by chromatographing on alumina 2.558 g (85%) of the pure starting 3,5-bis(trifluoromethyl)-α-nitrocumene (**7**) was obtained: mp 54–55 °C. Its NMR spectrum was identical with that of the starting material and it was pure by VPC. Clearly, inhibition had occurred.

Finally, the first experiment was repeated exactly as described above except that now it was conducted in a dark room and the reaction flask was wrapped with aluminum foil. The crude product was a pale tan viscous oil (3.185 g). VPC analysis showed that 69% of this oil was unreacted α-nitrocumene **7** and 31% was the β-arylated nitroparaffin **8**. The crude product was passed through a column of alumina and the resulting mixture was analyzed by VPC and by NMR. In this way it was found that 1.895 g of the resulting mixture was unchanged starting material (63% recovery) and that 0.963 g (28% yield) of the β-arylated nitroparaffin **8** was present. Thus this reaction will take place in the dark but at a distinctly slower rate than when exposed to two 20-W ordinary fluorescent lights.

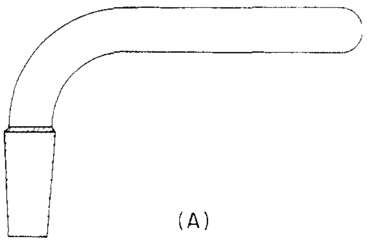


Figure 1. Addition tube (A).

2-Methyl-2-phenyl-3-nitrobutane. (A) Preparation. The reaction was carried out in a 25-mL three-neck flask according to the general procedure. Into one of the addition tubes (A) was placed 0.165 g (1 mmol) of α-nitrocumene and into the other addition tube was placed 0.162 g (2 mmol) of the lithium salt of nitroethane;[17] 10 mL of HMPA was placed in the flask. The HMPA was subjected to the freeze–pump–thaw procedure while the α-nitrocumene was kept frozen with dry ice. The contents of the two addition tubes were then transferred to the HMPA and the resulting mixture was stirred for 45 h under the light apparatus.[14] The yellow solution was then placed in an ice bath and an ice-cold solution of urea (0.369 g) in 1.8 mL of 20% acetic acid–80% water[18] was added all at once. The resulting solution was stirred for 10 min in the ice bath and then was poured into 200 mL of water containing ~2 g of NaCl. The cloudy aqueous HMPA solution was extracted repeatedly with pentane and the pentane extracts were then washed repeatedly with water. After drying over anhydrous $MgSO_4$ the pentane was removed on a rotary evaporator under reduced pressure. This gave 0.178 g of a colorless liquid which was separated into two fractions by preparative TLC (silica gel; 10% ethyl acetate–90% hexane). The first fraction (0.018 g) melted at 103–110 °C. On recrystallization from methanol 0.011 g (0.046 mmol; 9% yield) of 2,3-dimethyl-2,3-diphehylbutane was obtained: white needles; mp 116–117 °C (lit.[19] mp 118–119 °C); NMR ($CDCl_3$) δ 1.28 (s, 12 H), 7.15 (m, 10 H).

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30; mol wt, 238. Found: C, 90.65; H, 9.30; mol wt, 238.

The second fraction (0.152 g) was Kugelrohr distilled at 57 °C (0.01 mm), whereupon 0.143 g of a colorless liquid, $n^{22}{}_{D}$ 1.5200, was obtained; this is 2-methyl-2-phenyl-3-nitrobutane (74% yield). By TLC and VPC analysis this is a pure compound: NMR ($CDCl_3$) δ 1.29 (d, J = 7 Hz, 3 H), 1.44 (s, 6 H), 4.86 (q, J = 7 Hz, 1 H), 7.34 (m, 5 H); IR (neat) 6.52, 7.47 (NO_2) μm.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.01. Found: C, 68.14; H, 7.59; N, 7.25.

(B) The Effect of *m*-Dinitrobenzene. This experiment was a duplicate of the preceding one except that now a 25-mL four-neck flask containing three addition tubes (A) was used. The third addition tube contained 0.034 g (0.20 mmol) of *m*-dinitrobenzene and after the freeze–pump–thaw procedure this was added to the reaction mixture. Workup gave 0.178 g of a red liquid which on preparative TLC yielded 0.142 g of a pale yellow liquid. Kugelrohr distillation at 57 °C (0.1 mm) gave 0.135 g of a colorless liquid which NMR analysis reveals is a mixture of α-nitrocumene and 2-methyl-2-phenyl-3-nitrobutane in a ratio of 95:5. Thus, the 0.135 g of distillate corresponds to a 77% recovery of α-nitrocumene and a 4% yield of 2-methyl-2-phenyl-3-nitrobutane. The IR of this mixture is virtually identical with that of pure α-nitrocumene.

(C) The Effect of Di-*tert*-butyl Nitroxide. The first experiment of this group (A) was duplicated except that now a 50-mL four-neck flask containing three addition tubes was employed. The third addition tube contained 0.013 g (0.09 mmol) of di-*tert*-butyl nitroxide; during the freeze–pump–thaw deoxygenation procedure the nitroxide was kept frozen in dry ice to prevent loss by evaporation. Workup gave 0.169 g of a brown liquid from which, by preparative TLC, 0.133 g of a colorless liquid was obtained. Kugelrohr distillation at 57 °C (0.1 mm) gave 0.120 g (73% recovery) of α-nitrocumene. Its NMR, IR, and $n^{25}{}_{D}$ are identical with that of the starting material. TLC and VPC analyses also attest to the purity of this recovered α-nitrocumene.

(D) The Effect of Light. Experiment A of this group was repeated except that it was conducted in a dark room and the system was completely wrapped in aluminum foil. Workup, followed by the usual preparative TLC and Kugelrohr distillation, gave 0.137 g (83% recovery) of a colorless liquid which by NMR analysis consisted of α-nitrocumene contaminated by a trace (<2%) of 2-methyl-2-phenyl-3-nitrobutane. The IR spectrum and the $n^{25}{}_{D}$ of this material were identical with that of pure α-nitrocumene and the VPC and TLC analyses failed to reveal the presence of any impurity. Clearly, then, little if any reaction takes place in the dark in 45 h.

2-Methyl-2-*p*-cyanophenyl-3-nitrobutane (5). (A) Preparation. The reaction of *p*-cyano-α-nitrocumene[4] (0.190 g, 1 mmol) with 0.162 g (2 mmol) of the lithium salt of nitroethane[17] was carried out in 10 mL of HMPA according to the general procedure; a nitrogen purge was employed rather than the argon freeze–pump–thaw procedure. After 8 h the reaction flask was placed in an ice bath and a cold solution of 0.369 g (6 mmol) of urea dissolved in 1.8 mL of 20% acetic acid–80% water was added all at once. The solution was stirred for 10 min in an ice bath, after which it was poured into 200 mL of water containing ~2 g of NaCl. The aqueous HMPA solution was repeatedly extracted first with ethyl ether and then with benzene. The combined ether–benzene extracts were thoroughly washed with water and dried and then solvent was removed under reduced pressure. The 0.246 g of yellow liquid thus obtained was Kugelrohr distilled twice at 122 °C (0.1 mm). In this way 0.205 g (94% yield) of pure 2-methyl-2-(*p*-cyanophenyl)-3-nitrobutane (**5**) was obtained: mp 57–58 °C; NMR ($CDCl_3$) δ [1.4 (d, *J* = 7 Hz), 1.49 (s) 9 H], 4.82 (q, *J* = 7 Hz, 1 H), 7.4–7.8 (q, 4 H); IR (melt) 4.48 (C≡N), 6.48 (NO_2) μm.

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.84. Found: C, 65.83; H, 6.26; N, 12.64.

On standing for 3 weeks the melting point of 2-methyl-2-(*p*-cyanophenyl)-3-nitrobutane changed to 62–65 °C; the IR and NMR spectra of the higher melting material were, however, identical with those of the lower melting form. After 8 months the melting points had become 65–66 °C and an elemental analysis gave the following results: C, 66.28; H, 6.69; N, 12.98. Clearly, the higher melting material is a second crystalline form of 2-methyl-2-(*p*-cyanophenyl)-3-nitrobutane.

(B) The Effect of *m*-Dinitrobenzene. This experiment was a duplicate of the preceding one except that now an additional side-arm addition tube (A) was employed; it contained 0.034 g (0.2 mmol) of *m*-dinitrobenzene. After adding the lithium salt of nitroethane to the HMPA the *m*-dinitrobenzene was introduced and, finally, the *p*-cyano-α-nitrocumene. On workup 0.229 g of an orange solid, mp 46–55 °C, was obtained; this, on Kugelrohr distillation at 90 °C (0.1 mm), gave 0.172 of a yellow solid: mp 55–59 °C. Recrystallization from hexane produced 0.136 g (77% recovery) of white needles: mp 61–62 °C. That this is the pure starting material (*p*-cyano-α-nitrocumene) was further shown by a mixed melting point and by VPC and TLC. Finally, the recovered material and the starting material have identical NMR and IR spectra.

(C) The Effect of Di-*tert*-Butyl Nitroxide. The first experiment of this group (A) was repeated except that 0.014 g (0.1 mmol) of di-*tert*-butyl nitroxide (which was kept frozen during the nitrogen purge) was introduced prior to the addition of the *p*-cyano-α-nitrocumene to the HMPA. Workup gave 0.188 g of crude product: mp 57–58 °C. This after two Kugelrohr distillations at 90 °C (0.1 mm) was white and had: mp 60–61 °C; 0.172 g (91% recovery). Pure *p*-cyano-α-nitrocumene melts at 61–62 °C; the melting point of a mixture was 60.5–61.5 °C. The recovered material was identical by NMR, IR, VPC, and TLC with the pure starting material.

(D) The Effect of Light. Experiment A of this group was duplicated except that it was carried out in a dark room and the reaction system was wrapped in aluminum foil. The crude product (0.184 g) melted at 59–61 °C. Kugelrohr distillation at 90 °C (0.1 mm) gave 0.168 g (88% recovery) of white needles, mp 61–62 °C. The melting point of a mixture of this material and pure *p*-cyano-α-nitrocumene was 61–62 °C. The recovered material was identical by NMR, IR, VPC, and TLC with the starting material.

(E) Analytical Sensitivity. Mixtures of the starting compound (**4**) and the product (**5**) of these reactions (cf. eq 4) were analyzed by NMR in $CDCl_3$. In this way it was shown that at the 3% level 2-methyl-2-*p*-cyanophenyl-3-nitrobutane (**5**) can unequivocally be detected. Since NMR analyses of the crude reaction products of experiments B, C, and D of this group gave no evidence of the presence of **5** it can safely be concluded that in those experiments <3% was produced.

2,3-Dimethyl-2-(*p*-cyanophenyl)-3-nitrobutane. (A) Preparation. *p*-Cyano-α-nitrocumene[4] (9.50 g, 50 mmol), the lithium salt of 2-nitropropane[9,13] (23.75 g, 250 mmol), 500 mL of HMPA, a nitrogen atmosphere, and a reaction time of 50 h were employed. The crude reaction product (10.3 g) was a yellow solid, the NMR analysis of which indicated that it was contaminated with *p*-cyanocumyl dimer. On recrystallizations from methanol 8.01 g (68% yield) of 2,3-dimethyl-2-(*p*-cyanophenyl)-3-nitrobutane was obtained: mp 166–167 °C: NMR ($CDCl_3$) δ 1.53 (s, 12 H), 7.25–7.75 (m, 4 H).

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.14; H, 6.89; N, 11.93.

(B) Mechanistic Studies. The reaction of *p*-cyano-α-nitrocumene (**4**) with the lithium salt of 2-nitropropane was studied under argon using the freeze–pump–thaw technique (vide supra) to remove oxygen from the system. Each experiment of this set employed 0.190 g (1 mmol) of *p*-cyano-α-nitrocumene, 0.480 g (5 mmol) of the lithium salt of 2-nitropropane, 10 mL of HMPA, magnetic stirring, and a 36-h reaction time. Except for the dark experiment (see below) the reactions were conducted under the light apparatus.[14] The reaction mixture was poured into water containing sodium chloride and extracted with ether and benzene. The combined extracts were washed with water and dried and the solvents were removed under reduced pressure, thereby giving the crude product.

In the absence of inhibitors the crude product was a pale yellow solid (0.211 g): mp 133–155 °C. Kugelrohr distillation at 60 °C (0.1 mm) gave 0.012 g of a colorless, multicomponent liquid which was not further investigated. On raising the temperature to 100 °C a pale yellow solid (0.176 g) sublimed; on recrystallization from methanol 0.123 g of white plates were obtained: mp 167–168 °C. This is a 53% yield of pure 2,3-dimethyl-2-(*p*-cyanophenyl)-3-nitrobutane (**6**). On raising the temperature of the Kugelrohr oven to 131 °C (0.1 mm) a tan solid (0.019 g) sublimed over; two recrystallizations of this material from methanol yielded 0.010 g of a tan solid: mp 218–219 °C. The melting point of authentic 2,3-dimethyl-2,3-di(*p*-cyanophenyl)butane (the *p*-cyanocumyl dimer) is 218.5–220 °C.[20] From the NMR spectrum in $CDCl_3$[20] it appears that the 0.010 g of tan solid is a mixture of the *p*-cyanocumyl dimer and 2,3-dimethyl-2-(*p*-cyanophenyl)-3-nitrobutane (**6**) in the ratio 88:12. The presence of the *p*-cyanocumyl dimer was established by exact mass spectroscopy. Calcd exact mass, 288.163; found, 288.164.

A duplicate experiment in which 0.032 g (0.20 mmol) of *m*-dinitrobenzene was present gave 0.208 g of a red liquid as the crude product. Preparative TLC, followed by recrystallization from hexane, yielded 0.143 g (75% recovery) of pure *p*-cyano-α-nitrocumene (**4**): white needles; mp 61–62 °C. A mixed melting point was undepressed and the NMR and IR spectra were identical with those of the starting material.

A duplicate of the first experiment except that now 0.029 g (0.20 mmol) of di-*tert*-butyl nitroxide was present gave on workup 0.188 g of white crystals: mp 55–61 °C. By preparative TLC and recrystallization from hexane a total of 0.144 g (76%) of the starting *p*-cyano-α-nitrocumene (**4**) was recovered: mp 61–62 °C.

The final experiment of this group was a duplicate of the first except that it was conducted with complete exclusion of light. The crude product was a white solid: mp 58–62 °C. Kugelrohr distillation at 85 °C (0.1 mm), followed by preparative TLC and recrystallization from hexane gave 0.161 g (85% recovery) of pure *p*-cyano-α-nitrocumene: mp 61–62 °C.

2,3-Dimethyl-2-(*p*-cyanophenyl)-3-nitropentane. *p*-Cyano-α-nitrocumene[4] (1.90 g, 10 mmol), the lithium salt of 2-nitrobutane (5.45 g, 50 mmol), 100 mL of HMPA, the freeze–pump–thaw procedure, and a reaction time of 46 h were employed. The crude product was orange (2.72 g) and melted at 96–101 °C. It was Kugelrohr distilled at 100 °C (0.003 mm), whereupon 1.91 g of material, mp 103–106 °C, was obtained. This, on recrystallization from hexane gave 1.67 g (68% yield) of colorless crystals: mp 107–108 °C; NMR ($CDCl_3$) δ 0.82 (t, 3 H), 1.42 (s, 3 H), 1.51 (s, 6 H), 1.52 (m, 1 H), 2.37 (m, 1 H), 7.25–7.75 (m, 4 H).

Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.33; H, 7.60; N, 11.17.

2,3-Dimethyl-2-(*p*-benzenesulfonylphenyl)-3-nitrobutane. 4-Phenylsulfonyl-α-nitrocumene[4] (7.90 g, 26 mmol), the lithium salt of 2-nitropropane (26 g, 270 mmol), 250 mL of HMPA, under N_2, and a reaction time of 110 h were employed. Workup gave 10.1 g of an off-white solid, mp 135–139 °C, which after two recrystallizations from methanol melts at 143–143.5 °C (6.33 g; 71% yield): NMR ($CDCl_3$) δ 1.48 (s, 12 H), 7.33–7.63 (m, 5 H), 7.70–8.05 (m, 4 H).

Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 62.25; H, 6.05; N, 4.03; S, 9.22; mol wt, 347. Found: C, 61.98; H, 5.87; N, 3.86; S, 9.04; mol wt, 343.

2,3-Dimethyl-2-*m,m′*-bis(trifluoromethyl)phenyl-3-nitropentane. *m,m′*-Bis(trifluoromethyl)-α-nitrocumene[4] (3.40 g, 11.3 mmol), the lithium salt of 2-nitrobutane (6.15 g, 56.5 mmol), 80 mL of HMPA, the freeze–pump–thaw procedure, and a reaction time of 45 h were employed. The crude product was chromatographed on acid-washed alumina using cyclohexane and then benzene as eluents. Recrystallization from cyclohexane gave 2.0 g of colorless crystals (50% yield): mp 94–96 °C; NMR ($CDCl_3$) δ 0.83 (t, 3 H), 1.47 (s, 3 H), 1.58 (s, 6 H), 1.70 (m, 1 H), 2.36 (m, 1 H), 7.84 (s, 3 H); IR ($CHCl_3$) 6.54, 7.32, 7.85 μm.

For analysis a sample was sublimed: mp 94.5–96 °C.

Anal. Calcd for $C_{15}H_{17}NO_2F_6$: C, 50.42; H, 4.79; N, 3.92; F, 31.90. Found: C, 50.43; H, 4.77; N, 3.90; F, 31.95.

2,3-Dimethyl-2-(*p*-benzoylphenyl)-3-nitrobutane. 4-Benzoyl-α-nitrocumene[4] (2.69 g, 10 mmol), the lithium salt of 2-nitropropane (4.75 g, 50 mmol), 100 mL of HMPA, the freeze–pump–thaw procedure, and a reaction time of 72 h were employed. On workup 2.807 g of an orange solid, mp 95–100 °C, which NMR spectroscopy indicated was contaminated with *p*-benzoylphenylcumyl dimer, was obtained. Kugelrohr distillation at 120 °C (0.006 mm) gave 2.431 g of material: mp 102–104 °C. The pure product was obtained on recrystallization from a chloroform–hexane mixture: 1.915 g (62% yield) of colorless crystals; mp 109–110 °C; NMR ($CDCl_3$) δ 1.53 (s, 12 H), 7.3–7.9 (m, 9 H).

Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.35; H, 6.60; N, 4.48.

2,3-Dimethyl-2-(*p*-benzoylphenyl)-3-nitropentane. 4-Benzoyl-*α*-nitrocumene[4] (2.69 g, 10 mmol), the lithium salt of 2-nitrobutane[9,13] (5.45 g, 50 mm), 100 mL of HMPA, the freeze–pump–thaw procedure, and a reaction time of 74 h were employed. Workup yielded 3.31 g of an oil which, when Kugelrohr distilled at 120 °C (0.004 mm) gave 2.60 g of a pale yellow oil. Crystallization from hexane produced 1.92 g (61% yield) of colorless crystals: mp 93.5–94.5 °C; NMR ($CDCl_3$) δ 0.82 (t, 3 H), 1.43 (s, 3 H), 1.54 (s, 6 H), 1.60 (m, 1 H), 2.41 (m, 1 H), 7.3–7.9 (m, 9 H).

Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30; Found: C, 74.04; H, 7.10; N, 4.56.

2,3-Dimethyl-2-(*p*-nitrophenyl)-3-nitropentane. *α*,*p*-Dinitrocumene[4] (7.00 g, 35 mmol), the lithium salt of 2-nitrobutane[9,13] (19.07 g, 175 mmol), 350 mL of HMPA, a nitrogen atmosphere, and a 6-h reaction time were employed. The crude product (8.6 g; mp 99–105 °C) was recrystallized from a hexane–chloroform mixture. This gave 6.93 g (74% yield) of pure product: mp 105.5–106 °C; NMR ($CDCl_3$) δ 0.80 (t, 3 H), 1.42 (s, 3 H), 1.52 (s, 6 H), 1.56 (m, 1 H), 2.46 (m, 1 H), 7.52 (m, 4 H).

Anal. Calcd for $C_{13}H_{18}N_2O_4$: C, 58.64; H, 6.81; N, 10.52. Found: C, 58.85; H, 7.04; N, 10.47.

2,3-Dimethyl-3-(*p*-cyanophenyl)-2-nitropentane. 2-(*p*-Cyanophenyl)-2-nitrobutane (2.04 g, 10 mmol), the lithium salt of 2-nitropropane[9,13] (4.75 g, 50 mmol), 100 mL of HMPA, the freeze–pump–thaw procedure, and a reaction time of 92 h were employed. On workup 2.548 g of an orange oil was obtained; by NMR analysis the desired product was contaminated with 3,4-dimethyl-3,4-di(*p*-cyanophenyl)hexane. Kugelrohr distillation at 100 °C (0.004 mm) gave 1.977 g of a yellow oil which crystallizes from hexane: mp 71.5–72.5 °C; yield, 1.48 g (60%); NMR ($CDCl_3$) δ 0.69 (t, 3 H), 1.50 (s, 6 H), 1.56 (s, 3 H), 1.55–2.65 (m, 2 H), 7.25–7.80 (m, 4 H).

Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.47; H, 7.36; N, 11.14.

2,3-Dimethyl-3-*m*,*m*′-bis(trifluoromethyl)phenyl-2-nitropentane. 2-*m*,*m*′-Bis(trifluoromethyl)phenyl-2-nitrobutane (2.50 g, 7.95 mmol) and the lithium salt of 2-nitropropane[9,13] (3.77 g, 39.6 mmol) were allowed to react in 60 mL of HMPA. The freeze–pump–thaw procedure and a reaction time of 45 h were employed. The crude product was distilled in the Kugelrohr apparatus at 70–80 °C (1 mm); this gave 1.7 g of a colorless oil (60% yield): NMR ($CDCl_3$) δ 0.74 (t, 3 H), 1.55 (s, 9 H), 1.65–2.80 (m, 2 H), 7.78 (br s, 2 H), 7.86 (br s, 1 H); IR ($CHCl_3$) 6.52, 7.30, 7.82 μm.

Anal. Calcd for $C_{15}H_{17}NO_2F_6$: C, 50.42; H, 4.79; N, 3.92; F, 31.90. Found: C, 50.77; H, 5.00; N, 3.95; F, 31.85.

2,3-Dimethyl-3-(*p*-nitrophenyl)-2-nitropentane. 2-(*p*-Nitrophenyl)-2-nitrobutane[4] (9.85 g, 44 mmol), the lithium salt of 2-nitropropane (20.84 g, 220 mmol), 300 mL of HMPA, and a reaction time of 3 h were employed. The crude product was purified by chromatography on acid-washed alumina using benzene as the eluent. This was followed by recrystallization from hexane: yield 8.9 g (76%) of pale yellow crystals; mp 94–95.5 °C; NMR ($CDCl_3$) δ 0.72 (t, 3 H), 1.55 and 1.58 (s each, total 9 H), 1.72 (m, 1 H), 2.36 (m, 1 H), 7.50 and 8.19 (AA′BB′ system with J_{AB} = 9 Hz., total 4 H); IR ($CHCl_3$) 6.25, 6.58, 7.40 μm.

For analysis a small sample was again recrystallized from a cyclohexane–benzene mixture: mp 96–97 °C.

Anal. Calcd for $C_{13}H_{18}N_2O_4$: C, 58.64; H, 6.81; N, 10.52. Found: C, 58.78; H, 6.71; N, 10.30.

Solvent Effects. The effects of solvents on the reaction of *p*-cyano-*α*-nitrocumene (**4**) and of 3,5-bis(trifluoromethyl)-*α*-nitrocumene (**7**) with the lithium salt of 2-nitropropane were examined in a preliminary way. In both instances the reaction is much faster in HMPA than in Me_2SO or DMF. It is slowest in DMF, but the rate difference between DMF and Me_2SO is not large. Thus, in one set of experiments involving 4 when the reaction is 77% complete in HMPA it has proceeded only 26% in Me_2SO and 14% in DMF. Furthermore, the production of *p*-cyanocumyl dimer is highest in Me_2SO, next highest in DMF, and much the smallest in HMPA. Similar results were obtained in reactions employing **7**; the rate of reaction is unambiguously greater in HMPA than in the other two solvents. And here, again, the formation of cumyl dimer is minimal in HMPA.

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Registry No.—3,5-Bis(trifluoromethyl)nitrobenzene, 328-75-6; *N*-*α*-cumylformamide, 42044-69-9; *α*-methylstyrene, 98-83-9; *α*-aminocumene, 585-32-0; *m*,*m*′-bis(trifluoromethyl)cumyl dimer, 65253-47-6; 2,3-dimethyl-2,3-diphenylbutane, 1889-67-4; 2-methyl-2-(*p*-cyanophenyl)-3-nitrobutane, 65253-36-3; *p*-cyanocumyl dimer, 65253-48-7; *p*-cyanonitrobenzene, 619-72-7.

References and Notes

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(21) Fortunately, 2,3-dimethyl-2-phenyl-3-nitrobutane is readily obtained from 2,3-dimethyl-2-(*p*-nitrophenyl)-3-nitrobutane (cf. Table I) by reduction of the aromatic nitro group followed by replacement of the aromatic amino group by hydrogen (S. C. Carlson, unpublished work).