67-63-0; 2-methyl-1-butene, 563-46-2; cyclopentyl methyl ether, 5614-37-9; cyclooctyl methyl ether, 13213-32-6; cyclooctanol, 696-71-9; cyclooctene, 931-88-4; cyclohexyl methyl ether, 931-56-6; cyclohexyl ethyl ether, 932-92-3; *tert*-butyl cyclohexyl ether, 25246-83-7; mercuric trifluoroacetate, 13257-51-7; methanol, 67-56-1; ethanol, 64-17-5; *tert*-butyl alcohol, 75-65-0; 1-dodecene, 112-41-4; cyclopentene, 142-29-0; tetramethylethylene, 563-79-1; 1-hexene, 592-41-6; styrene, 100-42-5; *tert*-butylethylene, 558-37-2; cyclohexene, 110-83-8; norbornene, 498-66-8; 2-methyl-2-butene, 513-35-9.

Condensation–Cyclization of Carbanions with Electron-Deficient Aromatics. Formation and Structure of Delocalized Anions Containing the Bicyclo[3.3.1]nonane Skeleton

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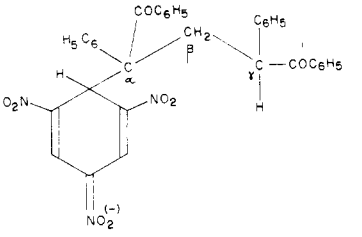
A series of new bicyclic anions containing the bicyclo[3.3.1]nonane skeleton have been prepared using *sym*-trinitrobenzene, ethyl 3,5-dinitrobenzoate, and picramide as the nitroaromatic moieties. Benzoylacetone, (*p*-nitrobenzoyl)acetone, (*m*-nitrobenzoyl)acetone, 1-(ethoxycarbonyl)-1-(X-benzyl)-2-propanone (X = H, *p*-OCH_3, *p*-CH_3, *p*-Cl, *p*-Br, *p*-NO_2 and *o*-NO_2), 1-(ethoxycarbonyl)-1-(2,3-dimethylbenzyl)-2-propanone, 1-(ethoxycarbonyl)-1-(1-naphthylmethyl)-2-propanone, and 1-(ethoxycarbonyl)-1-benzoyl-2-propanone have been utilized as the carbanion precursors. The condensation–cyclizations are initiated with triethylamine and piperidine. The cyclic adducts derived from (*p*-nitrobenzoyl)acetone and (*m*-nitrobenzoyl)acetone are identical due to loss of the nitrobenzoyl moiety. Similarly the adduct from the addendum 1-(ethoxycarbonyl)-1-benzoyl-2-propanone suffers cleavage of the benzoyl moiety. Observations on the steric effects caused by some substituents at the site of condensation and spectral characterizations of the bicyclics have been recorded.

A series of new bicyclic anions containing the bicyclo-[3.3.1]nonane skeleton has been prepared from TNB, 3,5-dinitrobenzonitrile, methyl 3,5-dinitrobenzoate, and carbanions derived from various ketones and keto esters such as acetone, acetylacetone, dicarbomethoxyacetone, and ethylacetoacetate, and a lactone (α-acetylbutyrolactone) by Strauss et al.[2]

No crystalline adduct has been prepared from TNB, benzoylacetone (1-benzoyl-2-propanone), and NEt_3. Interesting results in the kinetics of formation of this complex reported in the subsequent paper necessitated the isolation of the adduct. In the preparation of this adduct, the method of Strauss and co-workers[2] yielded only a pasty mass. In the present paper, a new procedure has been adopted to get a crystalline adduct **1** (see Experimental Section).

Attempts to prepare bicyclic adducts from TNB, NEt_3, and the compounds (*p*-nitrobenzoyl)acetone [1-(*p*-nitrobenzoyl)-2-propanone] and (*m*-nitrobenzoyl)acetone [1-(*m*-nitrobenzoyl)-2-propanone] under the same experimental conditions as for the formation of the adduct from benzoylacetone resulted in failure. Surprisingly, an unexpected product **2** resulted from both, but under different experimental conditions (see Experimental Section). Elemental analysis and visible, IR, and NMR spectra support structure **2**. It is noteworthy that this adduct **2** could not be obtained from TNB, acetone, and NEt_3.

Strauss et al.[3] have observed that in the presence of diethylamine the 1:1 Meisenheimer adduct of TNB–acetone cyclizes more rapidly than TNB–1,1-diphenylacetone and TNB–1,1,3,3-tetraphenylacetone adducts. The steric problems in the latter cases should be more severe than in the former. The same authors have reported that Meisenheimer adduct **3** fails to cyclize due to (i) two bulky groups C_6H_5 and COC_6H_5 at C_γ and (ii) hybridizational change of trigonal to tetrahedral at C_β. Previous



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studies in our laboratories[4] have established that α-bromo and ω-bromo acetoacetanilides do not form stable bicyclic adducts with TNB in the presence of NEt_3 due to the presence of a bulky bromine at the site of condensation. There have been only a few reports on steric effects at the C_γ position. The growing interest in examining the favorable conformation and conditions for cyclization promoted us to isolate a series of new adducts [**4–16**, Table I] from electron deficient aromatics and compounds of the type $CH_3COCHYZ$, where Y and Z are different substituents. A study of the kinetics of formation of the reported adducts is under progress and will form the subject matter of a later publication. The melting points, visible absorption maxima, and NMR data of the isolated adducts are listed in Table II.

Discussion

Benzoylacetone Adducts. In structure **2** the nitrobenzoyl moiety has cleaved off. This is probably due to

(1) To whom all inquiries should be addressed.
(2) Strauss, M. J.; Jensen, T. C.; Schran, H.; O'Conner, K. *J. Org. Chem.* **1970**, *35*, 383.
(3) Strauss, M. J.; Schran, H.; Taylor, S. P. B., unpublished results.
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0022-3263/85/1950-1174$01.50/0

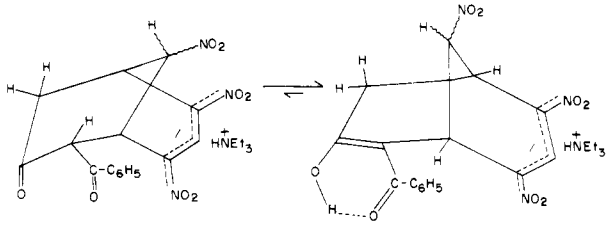
Table I

aromatic compd	amine	addendum	product
TNB	NEt_3	1-benzoyl-2-propanone	1, R = H; R′ = COC_6H_5
TNB	NEt_3	1-(*p*-nitrobenzoyl)-2-propanone or 1-(*m*-nitrobenzoyl)-2-propanone	2, R = R′ = H
TNB	NEt_3	1-benzyl-1-(ethoxycarbonyl)-2-propanone	4, X = H
TNB	NEt_3	1-(ethoxycarbonyl)-1-(*p*-methoxybenzyl)-2-propanone	5, X = *p*-OCH_3
TNB	NEt_3	1-(ethoxycarbonyl)-1-(*p*-methylbenzyl)-2-propanone	6, X = *p*-CH_3
TNB	NEt_3	1-(ethoxycarbonyl)-1-(*p*-chlorobenzyl)-2-propanone	7, X = *p*-Cl
TNB	NEt_3	1-(ethoxycarbonyl)-1-(*p*-bromobenzyl)-2-propanone	8, X = *p*-Br
TNB	NEt_3	1-(ethoxycarbonyl)-1-(*p*-nitrobenzyl)-2-propanone	9, X = *p*-NO_2
TNB	NEt_3	1-(ethoxycarbonyl)-1-(*o*-nitrobenzyl)-2-propanone	10, X = *o*-NO_2
TNB	NEt_3	1-(2,3-dimethylbenzyl)-1-(ethoxycarbonyl)-2-propanone	11
TNB	NEt_3	1-(ethoxycarbonyl)-1-(1-naphthylmethyl)-2-propanone	12
TNB	$C_5H_{10}NH$	1-benzyl-1-(ethoxycarbonyl)-2-propanone	13
ethyl 3,5-dinitrobenzoate	NEt_3	1-benzyl-1-(ethoxycarbonyl)-2-propanone	14
picramide	NEt_3	1-benzyl-1-(ethoxycarbonyl)-2-propanone	15
TNB	NEt_3	1-benzoyl-1-(ethoxycarbonyl)-2-propanone	16, R = H; R′ = COOEt

attack of C_2H_5OH on the positive carbonyl adjacent to the phenyl ring, now rendered very highly positive by the *m*- and *p*-nitro groups, followed by cleavage of the methine–carbonyl bond adjacent to the nitrophenyl group of adduct **2a** as shown in Scheme I.

While the broad carbonyl absorption frequency of (*p*-nitrobenzoyl)acetone occurs at 1570–1620 cm^{-1} due to enolization, a sharp absorption band at 1720 cm^{-1} is observed in the IR spectrum of adduct **2**. This indicates a free carbonyl group which is not involved in enolization. The above observation and the fact that no peak is present around δ 7.3 in the NMR spectrum of **2** support that the nitrobenzoyl moiety of (*p*-nitrobenzoyl)acetone has cleaved off in the isolated complex.

There is no appreciable absorption above 1660 cm^{-1} in the IR spectrum of the adduct from benzoylacetone (**1**) presumably because the β-diketo function exists to a considerable extent in the enol form (**1b**). The weak absorption at 1710 cm^{-1} is probably due to a trace of the diketo form **1a**.

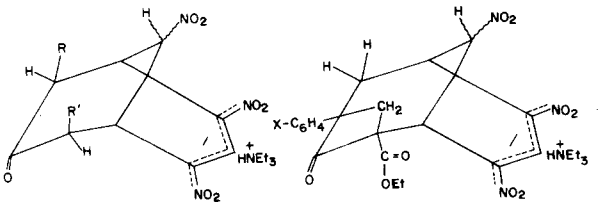


1a 1b

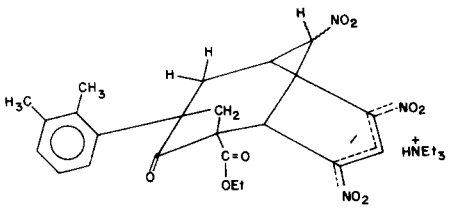
Since exchange with Me_2SO-d_6 is a complicating factor, enolic absorptions are difficult to detect in the NMR spectra determined in this solvent. Other observed NMR results of the adducts **1** and **2** are presented in Table II.

Adducts from the Addenda of the Type $CH_3COCHYZ$. Addition of excess NEt_3 to a solution of 1-cyano-1-phenyl-2-propanone [$C_6H_5CH(CN)COCH_3$] and TNB in Me_2SO–EtOH (50% v/v)] resulted initially in a solution with absorption maxima at 465 and 560 nm, characteristic of a 1:1 Meisenheimer adduct, which was stable only for a few minutes in solution. Repeated attempts to isolate the Meisenheimer and bicyclic adducts from this ketone failed. This is presumably because the equilibrium lies far on the side of the reactants due to the presence of two groups (C_6H_5 and CN) at the site of condensation.

Though 1-benzyl-1-(ethoxycarbonyl)-2-propanone [$C_6H_5CH_2CH(COOEt)COCH_3$] has two substituents at the site of condensation, it forms stable bicyclic adducts with electron deficient aromatics such as TNB, ethyl 3,5-dinitrobenzoate, and picramide in the presence of NEt_3 or piperidine. Stable bicyclic adducts result when the phenyl group of 1-benzyl-1-(ethoxycarbonyl)-2-propanone carries OCH_3, CH_3, Cl, Br, or NO_2 groups (**5–10**) and also when the benzyl group is replaced by an α- naphthylmethyl group (**12**).



1, 2, & 16 4 – 10



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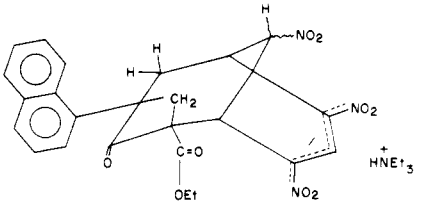

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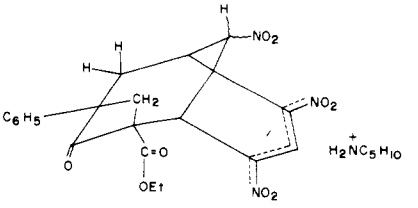

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The complexes from TNB are red in color while those from ethyl 3,5-dinitrobenzoate and picramide are yellow due to changes in the structure of the delocalized pro-

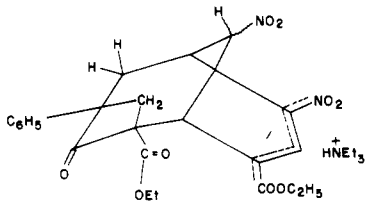
Table II. Physical and Spectral Data for Bicyclic Anions 1, 2, and 4–16[a]

no.	mp, °C	λ_{max}, nm (C_2H_5OH)	proton type: propenide	bridgehead	bridging $HCNO_2$	aromatic	other
1	143	506	8.4 (s, 1 H)	4.35 (m, 1 H), 4.55 (m, 1 H)	5.7 (t, 1 H, J = 3 Hz)	7.4–8.2 (m, 5 H)	α to keto bridge obscured by cation absorption
2	137	508	8.37 (s, 1 H)	4.37 (m, 2 H)	5.69 (t, 1 H, J = 3 Hz)		α to keto bridge 2.3–3.0 (m, 4 H)
4	131	506	8.47 (s, 1 H)	4.25 (m, 1 H), 5.15 (m, 1 H)	5.45 (t, 1 H, J = 4 Hz)	7.12 (s, 5 H)	(i) α to keto bridge under cation absorption (ii) 0.85 (t, 3 H, J = 8 Hz), 3.77 (q, 2 H), COOEt
5	130	507	8.37 (s, 1 H)	4.22 (m, 1 H), 5.15 (m, 1 H)	5.47 (t, 1 H, J = 3.5 Hz)	6.65, 7.07 (dd, J = 8 Hz each, 4 H)	(i) α to keto bridge under cation absorption (ii) 0.97 (t, 3 H, J = 8 Hz), 3.77 (q, 2 H), COOEt
6	132	508	8.55 (s, 1 H)	4.35 (m, 1 H), 5.35 (m, 1 H)	5.51 (t, 1 H, J = 3.5 Hz)	6.97, 7.13 (dd, J = 6 Hz each, 4 H)	(i) α to keto bridge under cation absorption (ii) 0.85 (t, 3 H, J = 8 Hz), 3.7 (q, 2 H), COOEt
7	123	509	8.5 (s, 1 H)	4.32 (m, 1 H), 5.22 (m, 1 H)	5.52 (t, 1 H, J = 3.5 Hz)	7.15, 7.32 (dd, J = 6.5 Hz each, 4 H)	(i) α to keto bridge under cation absorption (ii) 0.92 (t, 3 H, J = 8 Hz), 3.85 (q, 2 H) COOEt
8	128	507	8.47 (s, 1 H)	4.27 (m, 1 H), 5.17 (m, 1 H)	5.45 (t, 1 H, J = 3.5 Hz)	7.07, 7.30 (dd, J = 8.5 Hz each, 4 H)	(i) α to keto bridge under cation absorption (ii) 0.92 (t, 3 H, J = 7 Hz), 3.80 (q, 2 H) COOEt
9	160	505	8.50 (s, 1 H)	4.36 (m, 1 H), 5.27 (m, 1 H)	5.42 (t, 1 H, J = 3.5 Hz)	7.47, 8.05 (dd, J = 9.5 Hz each, 4 H)	(i) α to keto bridge under cation absorption (ii) 0.95 (t, 3 H, J = 8 Hz), 3.90 (q, 2 H) COOEt
10	132	504	8.50 (s, 1 H)	4.32 (m, 1 H), 5.25 (m, 1 H)	5.52 (t, 1 H, J = 4 Hz)	7.30–8.10 (m, 4 H)	(i) α to keto bridge under cation absorption (ii) 0.97 (t, 3 H, J = 8 Hz), 3.92 (q, 2 H) COOEt
11[b]	120	508	8.10 (s, 1 H)	4.13 (m, 1 H), 4.97 (m, 1 H)	5.30 (t, 1 H, J = 3 Hz)	6.67 (s, 3 H)	(i) α to keto bridge under cation absorption (ii) 0.90 (t, 3 H, J = 6 Hz), 3.65 (q, 2 H) COOEt
12	127	505	8.59 (s, 1 H)	4.34 (m, 1 H), 5.52 (m, 1 H) overlaps bridging proton	5.52 (m, 1 H, overlaps with bridgehead proton	7.29–8.34 (m, 7 H)	(i) α to keto bridge under cation absorption (ii) 0.49 (t, 3 H, J = 8 Hz), 3.15 (q, 2 H, overlaps cation absorption)
13[b]	132	507	8.15 (s, 1 H)	4.15 (m, 1 H), 5.05 (m, 1 H)	5.21 (t, 1 H, J = 3.5 Hz)	6.90 (s, 5 H)	(i) α to keto bridge under cation absorption (ii) 0.90 (t, 3 H, J = 6 Hz), 3.65 (q, 2 H) COOEt
14[b]	162	383	7.65 (s, 1 H)	4.35 (m, 1 H), 4.47 (m, 1 H)	5.20 (t, 1 H, J = 3 Hz)	6.90 (s, 5 H)	α to keto bridge under cation absorption
15[b]	134	421		4.20 (m, 1 H), 5.05 (m, 1 H)	5.40 (t, 1 H, J = 3.5 Hz)	6.90 (s, 5 H)	(i) α to keto group under cation absorption (ii) 0.90 (t, 3 H, J = 6 Hz), 3.70 (q, 2 H) COOEt (iii) 10.40 (br, 2 H) NH_2
16[c]	147–148	504	8.40 (s, 1 H)	4.30 (br, 2 H)	5.20 (t, 1 H, J = 3 Hz)		α to keto group under cation absorption

[a] The NMR data were measured at 60 MHz and chemical shifts are given as δ values. The following abbreviations for proton splittings are used: s = singlet; dd = double doublet; t = triplet; q = quartet; m = multiplet; br = broad. [b] Measured at 90 MHz. [c] Reference 2.

penide portion. Similar color changes have been noticed by Strauss et al.[2] The IR spectra of all adducts (4–15) have strong absorption bands at ~1715 cm^{-1} supporting the diketo structure. In the IR spectrum of adduct 14 two strong bands are observed at 1715 and 1680 cm^{-1}. The latter absorption must be due to the carbonyl group of the $COOC_2H_5$ attached to the delocalized propenide function. The propenide protons in the adducts (4–13 and 16) appear as a singlet at ~8.4 ppm, whereas that of adduct 14 appears at 7.65, 0.75 ppm upfield from that in the trinitro adducts, again indicating that the less electron withdrawing $COOC_2H_5$ group is part of the delocalized anionic portion.

No bicyclic adduct from picramide has been reported so far. The IR spectrum of the adduct from picramide 15 has a strong band at 1710 cm^{-1} for free keto groups. a band at 2650 cm^{-1} is caused by hydrogen bonded NH_2. In the NMR spectrum, the peak due to two NH_2 protons appears at δ 10.4.



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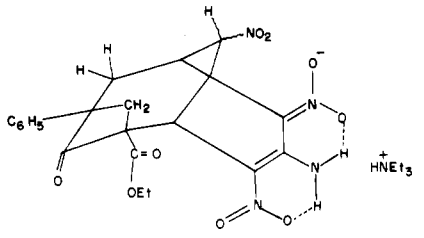


15

Attempts have been made to isolate a bicyclic adduct from TNB, 1-benzoyl-1-(ethoxycarbonyl)-2-propanone [$C_6H_5COCH(COOEt)COCH_3$], and NEt_3 by adopting the procedure cited in the Experimental Section and resulted in **16**. Formation of **16** can be accounted for in terms of cleavage, as referred to, in the formation of **2**.

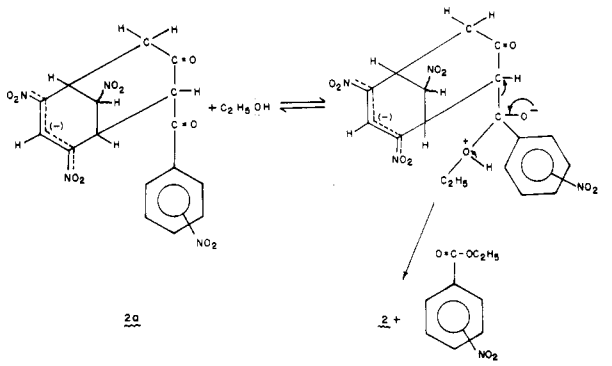
Experimental Section

General Methods. All melting points are uncorrected. The visible data were obtained on a Carl-Zeiss UV–vis specord. The NMR data were recorded on a Varian T-60 (60 MHz) and EM-390 (90 MHz) spectrometer with Me_2SO-d_6 as solvent and Me_4Si as an internal reference. The IR spectra were recorded on a Perkin-Elmer 599 infrared spectrophotometer as KBr pellets.

Benzoylacetones were prepared from the corresponding acetophenones and acetic anhydride by using boron trifluoride.[5] 1-Cyano-1-phenyl-2-propanone and 1-benzoyl-1-(ethoxycarbonyl)-2-propanone were prepared respectively by known procedures.[6,7] 1-(Ethoxycarbonyl)-1-(X-benzyl)-2-propanones were prepared from corresponding benzylchlorides and the sodium salt of ethylacetoacetate.[8]

Preparation of Adduct 1. TNB (0.01 mol) was ground with benzoylacetone (0.01 mol) in a mortar. To this mull a two- to three-fold excess of NEt_3 was added and again ground well. The greenish, tarlike mixture was kept at 30 °C under vacuum for 24 h. The tarlike mass was repeatedly washed with anhydrous ether and finally extracted with hot chlorofrom. The extract was concentrated under reduced pressure to 10–15 mL. The resultant slurry was added to 75 mL of anhydrous ether, and the mixture was cooled in a calcium chloride–ice bath for two days. The orange crystals were collected and recrystallized from hot chlorofrom (yield 40%).

Scheme I



2a

Preparation of Adducts 2 and 4–16. These adducts were prepared by dissolving the electron deficient aromatic (0.01 mol) and addendum (0.01 mol) in ethanol to give a saturated solution. A two- to three-fold excess of amine was added, and the intensely colored solution was kept at 25–30 °C for 24 h. The solution was concentrated under vacuum giving an oily mass. The oil was washed with copious amounts of anhydrous ether and redissolved in ether–ethanol solution which, after standing for 12 h at 0–10 °C, deposited crystals of the adduct. Adducts were recrystallized twice from absolute ethanol. The yield of the complex is 50–60% in all the cases. All the complexes gave satisfactory elemental analyses.

Acknowledgment. We gratefully acknowledge the help rendered by Dr. Kurt L. Loening, Director of Nomenclature, The American Chemical Society, in the nomenclature of the compounds. We thank Dr. M. V. Bhatt, I. I. Sc, Bangalore, for the NMR and IR spectra. Our thanks are due to Dr. P. Shanmugam, Bharathiar University, Coimbatore, Dr. R. Balasubramanian, University of Madras, and Dr. S. Selvavinayakam, CIBA-GEIGY Research Centre, Bombay, for the micro analyses. We are very grateful to the Department of Science and Technology, Government of India, for a research grant.

Registry No. **1**, 95314-37-7; **2**, 95314-38-8; **4**, 95314-40-2; **5**, 95314-42-4; **6**, 95314-44-6; **7**, 95314-46-8; **8**, 95314-48-0; **9**, 95314-50-4; **10**, 95314-52-6; **11**, 95314-54-8; **12**, 95314-56-0; **13**, 95314-57-1; **14**, 95314-59-3; **15**, 95344-29-9; **16**, 30485-32-6; NEt_3, 121-44-8; $C_5H_{10}NH$, 110-89-4; 2,4,9-trinitro-6-phenyl-6-cyanobicyclo[3.3.1]non-2-en-7-one, 95344-27-7; 1-(*m*-nitrobenzoyl)-2-propanone, 5435-66-5; 1-(ethoxycarbonyl)-1-(*p*-methoxybenzyl)-2-propanone, 36600-75-6; 1-(ethoxycarbonyl)-1-(*p*-methylbenzyl)-2-propanone, 14305-31-8; 1-(ethoxycarbonyl)-1-(*p*-chlorobenzyl)-2-propanone, 36600-72-3; 1-(ethoxycarbonyl)-1-(*p*-bromobenzyl)-2-propanone, 95314-60-6; 1-(ethoxycarbonyl)-1-(*p*-nitrobenzyl)-2-propanone, 61713-40-4; 1-(ethoxycarbonyl-1-(*o*-nitrobenzyl)-2-propanone, 95314-61-7; 1-(2,3-dimethylbenzyl)-1-(ethoxycarbonyl)-2-propanone, 95314-62-8; 1-(ethoxycarbonyl)-1-(1-naphthylmethyl)-2-propanone, 88022-93-9; 1-benzoyl-1-(ethoxycarbonyl)-2-propanone, 569-37-9; 1-cyano-1-phenyl-2-propanone, 4468-48-8; benzoylacetone, 93-91-4; 1-(*p*-nitrobenzoyl)-2-propanone, 4023-82-9; 1-benzyl-1-(ethoxycarbonyl)-2-propanone, 620-79-1; 1,3,5-trinitrobenzene, 99-35-4; ethyl 3,5-dinitrobenzoate, 618-71-3; picramide, 489-98-5.

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