by ammonium sulfate precipitation contained amylase and therefore lost their glycogen. With such enzymes no UDP formation took place unless a primer was added. As shown in Table II glycogen and soluble starch acted as primers whereas glucose and maltose were ineffective. Several mono-, di- and oligosaccharides and hexose phosphates were tested with negative results. Treatment of glycogen with α-amylase destroyed its priming capacity. It can be concluded that UDPG acts directly as a glucose donor to glycogen and that the reaction is thus similar to polysaccharide formation from glucose 1-phosphate with animal phosphorylase which requires a primer of high molecular weight. The enzyme was found in the soluble fraction of liver and became very unstable after purification.

TABLE II

PRIMER REQUIREMENT

System as in Table I, but glycogen omitted. The enzyme (0.01 ml.) was obtained by precipitation with 1.6 *M* ammonium sulfate followed by dialysis. Incubated 60 min. at 37°.

Additions	ΔUDP (μmoles)
None	0
0.1 mg. glucose	0
0.2 mg. maltose	0
0.4 mg. glycogen	0.08
0.4 mg. soluble starch	0.06

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RECEIVED OCTOBER 23, 1957

DETONATION OF LIQUID OXYGEN–LIQUID METHANE SOLUTIONS

Sir:

The classical theory of detonation was developed from the study of simple explosive *gas* mixtures, such as: $H_2 + O_2$, $CO + O_2$, or $CH_4 + O_2$. The study of the same systems, in *liquid* or *solid* phase, has, however, not been undertaken to our knowledge. In connection with this Institute's high temperature research, it was found that liquid CO and CH_4 form clear homogeneous solutions with liquid O_2 over the whole composition range from 0 to 100% O_2. They are colorless on the CH_4- or CO-rich side and gradually approach the color of liquid O_2 on the O_2-rich side. They detonate with great brisance.

These mixtures, as well as others, such as liquid hydrogen and solid oxygen powder, solid cyanogen powder and liquid oxygen, liquid or solid ozone, lead to very simple detonation products. In many cases only *individual compounds* are formed (*i.e.*, $2\,CO + O_2 \longrightarrow$ only CO_2, $O_3 \longrightarrow$ only O_2, $2\,H_2 + O_2 \longrightarrow$ only H_2O) in contrast to the usual condensed explosives like TNT, tetryl, PETN, nitroglycerine, etc., (*i.e.*, TNT $\longrightarrow$ CO_2, CO, $C_{sol.}$, H_2O, H_2, N_2 and some CH_4). Thus an opportunity is provided to study, both experimentally and theoretically, *single compounds* or very simple mixtures in a region of temperatures and pressures far beyond the usual.

The preliminary detonation velocities shown in Table I were obtained with CH_4(liq.)–O_2(liq.) mixtures, using the rotating mirror equipment of the Naval Ordnance Laboratory. The mixtures were prepared in Dewar flasks in quantities of $\simeq$500 cc. by mixing desired amounts of liquid O_2 and CH_4, and their detonation was initiated by an electric blasting cap and a plane wave booster with tetryl and RDX composition B.

The maximum detonation velocity for the *gas* systems is reached with the 1:1 molar mixture. The *liquid* maximum is close to the composition

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

This corresponds to the maximum energy release (see Table I) and could be anticipated since the high detonation pressure (calcd. $\simeq 6.8 \times 10^4$ atm.), stabilizes both the CO_2 and H_2O molecules, which dissociate at the high temperature and low pressure of the gaseous system.

The theoretical values have been calculated using standard procedures[1] and are substantially higher than our experimental results. Small amounts (1–2%) of N_2 which conceivably may have dissolved in our mixtures, cannot account for this discrepancy.

Additional measurements with the simplest possible systems, *i.e.*, $(CO)_{liq.} + (O_2)_{liq.}$ and pure O_3, as well as their theoretical study, are desirable to explain the above discrepancy.

TABLE I

Molar ratio O_2:CH_4	ΔE 90°K., kcal./mole	Liquid density at 90°K., g./cm.^{3}	Exptl. Detonation velocity, m./sec. Gas at 300°K.	Exptl. Detonation velocity, m./sec. Liq. at 90°K.	Calcd. values for liquid system Detonation velocity, m./sec.	Calcd. values for liquid system Detonation temp., °K.	Calcd. values for liquid system Detonation pressure $\times 10^{-4}$, atm.
4.00	173.10	0.980	2075[a]	3325	4400	4150	8.1
2.00	180.18	.879	2322[b]	5120	6010	5830	6.8
1.50	114.10	.830	2470[b]	5110	5840	4670	5.0
1.00	57.85	.755	2528[b]	4615	5250	3040	2.9

[a] R. B. Morrison, Univ. of Michigan, Report UMM-97, Jan. 1952, p. 99. [b] B. Lewis and G. von Elbe, "Combustion, Flames and Explosion of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 584. (H. B. Dixon's data 1894, 1903.)

The liquid system was found to detonate at least in the range from 11 to 67 mole % CH_4, while the inflammability range of the gas system is 5.4 to 59.2 mole % CH_4.

We wish to thank the Office of Ordnance Research for its financial support, and the Naval Ordnance Laboratory and their Dr. S. J. Jacobs

(1) J. Taylor, "Detonation in Condensed Explosives," The Clarendon Press, Oxford, England, 1952, pp. 87–110.

and Mr. N. Coleburn for the use of their facilities and for their help.

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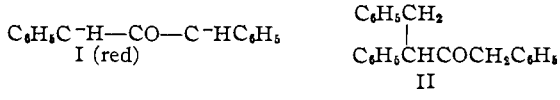
RECEIVED OCTOBER 8, 1957

DICARBANIONS OF DIBENZYL KETONE, DIBENZYL SULFONE AND α,β,β-TRIPHENYLPROPIONITRILE

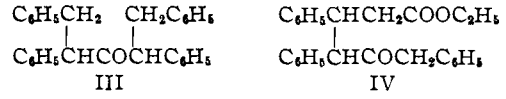
Sir:

We have observed that dibenzyl ketone is converted by two equivalents of potassium amide in liquid ammonia to a dark red dicarbanion I, the basic and nucleophilic strength of which is evidently much greater than that of the common colorless monocarbanion of this ketone. Thus, whereas the monocarbanion produced a mixture of products with benzyl chloride, the dicarbanion I reacted rapidly with a molecular equivalent of this halide to form, after acidification, a high yield of the monoalkylation product II, m.p. 72–73.5° (lit. m.p. 74–74.5°).[1]



I (red) II

Dicarbanion I gave with two molecular equivalents of benzyl chloride a good yield of dialkylation product III (apparently one diastereoisomer), m.p. 120.5–122° (lit. m.p. 121°),[2] *Anal.* Calcd. for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 89.07; H, 6.42.

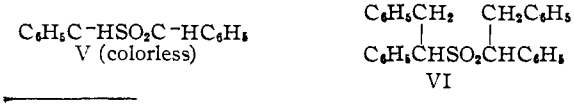


III IV

Although the monocarbanion of dibenzyl ketone failed to react appreciably with ethyl cinnamate in liquid ammonia during 0.5 hour, dicarbanion I rapidly underwent conjugate addition with a molecular equivalent of this α,β-unsaturated ester to form, after acidification, an excellent yield of ketone-ester IV (apparently a mixture of *threo* and *erythro* isomers). A recrystallized sample (m.p. 149–149.5°) was analyzed. *Anal.* Calcd. for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.65; H, 6.71.

Saponification of IV gave a good yield of the corresponding acid, m.p. 231.5–233.5° (apparently a single isomer). *Anal.* Calcd. for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.55; H, 5.87.

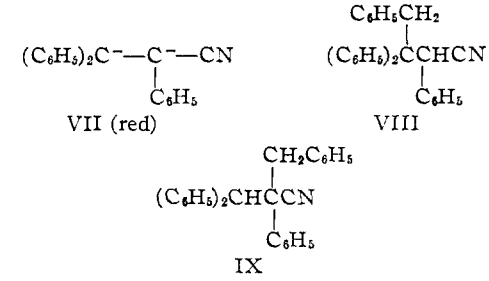
Similarly dibenzyl sulfone was converted by two equivalents of potassium amide in liquid ammonia to dicarbanion V (colorless) which reacted with two molecular equivalents of benzyl chloride to form a good yield of the dialkylation product VI, m.p. 187.5–188.5° (apparently one diastereoisomer). *Anal.* Calcd. for $C_{28}H_{26}SO_2$: C, 78.85; H, 6.14; S, 7.50. Found: C, 79.07; H, 5.97; S, 7.61.



V (colorless) VI

(1) A. McKenzie and R. Roger, *J. Chem. Soc.*, 571 (1927).
(2) C. Rattner, *Ber.*, **21**, 1316 (1888).

Also, α,β,β-triphenylpropionitrile was converted by two equivalents of potassium amide in liquid ammonia to a dark red dicarbanion VII, which apparently reacted preferentially at the β-position with a molecular equivalent of benzyl chloride to form, after acidification, a high yield of the monoalkylation product VIII, m.p. 125.5–128.5°. *Anal.* Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.02; H, 6.25; N, 3.81.



VII (red) VIII

IX

The common type of monobenzylation of α,β,β-triphenylproprionitrile at the α-carbon atom was effected by means of an equivalent of potassium amide to form IX, m.p. 185.5–187° which is isomeric with VIII. *Anal.* Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.14; H, 6.33; N, 3.88.

Studies on related condensations of multiple carbanions are in progress.

(3) National Science Foundation Predoctoral Fellow 1956-1958.

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γ-(3-PYRIDYL)-γ-METHYLAMINOBUTYRIC ACID AS A URINARY METABOLITE OF NICOTINE[1]

Sir:

Studies in the rat[2] and dog[3] with uniformly labelled-C^{14} (−)-nicotine have shown that virtually all of the administered radioactivity is excreted in the urine. In the dog, approximately 10% of the excretion was unchanged nicotine with the remainder distributed[4] between seven chromatographically distinct fractions.

We wish to report the first chemical identification of a compound obtained from the metabolism of nicotine in the intact animal.

A sample of 18-hour pooled urine from six dogs which had received nicotine (10 mg./kg. intravenously) portionwise under pentobarbital anesthesia during an 8-hour period was adjusted to *p*H 2 with 5 *N* HCl. The solution was placed on Dowex 50 × 4 (H+ form). After a water wash, material giving a positive Koenig reaction was eluted with 1 *N* ammonia water. The aqueous solution of the residue from the vacuum concentration of this fraction was extracted with chloroform and then at *p*H 10–11 placed on Dowex 1

(1) Appreciation is expressed for support of this work by the Tobacco Industry Research Committee and The American Tobacco Company.
(2) A. Ganz, F. E. Kelsey and E. M. K. Geiling, *J. Pharmacol. Exp. Therap.*, **103**, 209 (1951).
(3) D. R. Bennett, R. E. Tedeschi and P. S. Larson, *Arch. int. pharmacodyn.*, **98**, 221 (1954).
(4) F. B. Owen, Jr., and P. S. Larson, *ibid.*, in press.